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PHOSPHORUS

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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PHOSPHORUS

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor any other group.

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1 SUMMARY

WHITE (YELLOW) PHOSPHORUS (P_4)

Colourless or white to pale yellow solid, waxy appearance

SYNONYMS

Yellow Phosphorus, White Phosphorus, Phosphorus Yellow, Phosphorus White, Phosphorus White Dry, Phosphorus Yellow Dry, Phosphore Blanc (Fr.)

IDENTIFICATION NUMBERS

UN No. 1381 (dry or in water), 2447 (molten); CAS No. 12185-10-3; OHM-TADS No. 7216854; STCC No. 4916140 (yellow or white), 4916141 (in water)

GRADES & PURITIES

Commercial: 99.9 percent

IMMEDIATE CONCERNS

Fire: Ignites spontaneously upon contact with air. Intense white fumes of highly irritating P_4O_{10} are released as well as some lower oxides of phosphorus and considerable heat

Human Health: Highly toxic by all routes

Environmental: Acute and chronic effects on aquatic biota are significant at concentrations well below 10 µg/L. Available data indicate an environmentally safe concentration should be equal to or less than 0.01 µg/L as P_4

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): solid
Boiling Point: 280.5°C
Melting Point: 44.1°C
Flammability: ignites spontaneously in air
Specific Gravity: 1.82 (20°C)
Solubility (in water): very slightly soluble
Behaviour (in water): sinks, with slight dissolution
Behaviour (in air): ignites, forming fume cloud of primarily P_4O_{10} and producing considerable heat
Odour Threshold: odourless

ENVIRONMENTAL CONCERNS

Toxic to aquatic life in very low concentrations. Subject to bioaccumulation. There is no demonstrated potential for food chain contamination in the sense of that by pesticides.

HUMAN HEALTH

TLV: 0.1 mg/m^3 (inhalation)

Exposure Effects

Inhalation of Combustion Products: Irritation of respiratory tract, skin and eyes

Inhalation of Solid Phosphorus: Photophobia with myosis, dilation of pupils, retinal hemorrhage and congestion of blood vessels

Ingestion: Vomiting, weakness, necrosis of the mandible, anemia, loss of appetite, pallor

Contact: Will cause severe burns to skin and eyes

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "SPONTANEOUSLY FLAMMABLE; POISON". Call fire department and notify manufacturer/shipper. Eliminate all nonessential personnel. Avoid contact with solid or liquid and inhalation of fumes from combustion. Stay upwind. Minimize escape of phosphorus. Stop leak, if possible without risk, or cool container to solidify contents. Collect contaminated water for subsequent recovery. Wear firefighters' full protective clothing and self-contained breathing apparatus.

Fire Control

Wear firefighters' full protective clothing and self-contained breathing apparatus. Use water spray or fog to extinguish. Foam is effective, dry chemical is not. Cover small fire with water, wet sand, or earth. Cool fire-exposed containers with water. Remove exposed containers from fire area, if possible without risk.

COUNTERMEASURES

Emergency Control Procedures in/on:

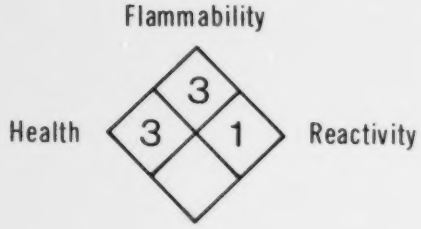
Soil: Construct earth barriers to contain spill and cover with water, wet sand, or soil to prevent ignition or to extinguish. Remove material by manual or mechanical means, taking care not to expose solid to air. Place in containers, cover with water or wet sand and seal with appropriate cover/lid

Water: Contain by forming deep natural water pockets or sand bag barriers. Remove trapped material by mechanical means, e.g., shovels, dredges, etc.

NAS HAZARD RATING

Category	Rating
Fire	3
Health	
Vapour Irritant	N/A
Liquid or Solid Irritant	4
Poison	4
Water Pollution	
Human Toxicity	3
Aquatic Toxicity	4
Aesthetic Effect	1
Reactivity	
Other Chemicals	4
Water	0
Self-reaction	0

NFPA
HAZARD
CLASSIFICATION



RED PHOSPHORUS (P_x)

Reddish-brown amorphous powder or red to violet crystals

SYNONYMS

Amorphous Red Phosphorus, Phosphorus, Red (Amorphous)

IDENTIFICATION NUMBERS

UN No. 1338; CAS No. 7723-14-0; OHM-TADS No. 7216855; STCC No. 4916725 (red), 4916142 (red and yellow)

GRADES & PURITIES

Technical: 98 percent minimum

IMMEDIATE CONCERNS

Fire: Heat may cause reversion to white phosphorus which ignites spontaneously upon contact with air. Ignites at 260-280°C

Human Health: Reported to be of low toxicity by all routes; however, no literature is available to corroborate this statement

Environmental: Reported to be of low toxicity to aquatic life and animals although no significant studies have been found to verify this assumption

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): solid
Boiling Point: ignites at 260-280°C
Melting Point: 590°C (4.4×10^3 kPa), sublimes at 416°C
Flammability: combustible solid
Density: 2340 kg/m^3 (crystal), 2160 kg/m^3 (amorphous)
Solubility (in water): insoluble
Behaviour (in water): sinks, very slow reaction
Odour Threshold: odourless

ENVIRONMENTAL CONCERNS

Considered virtually nontoxic; however, details are not certain as data are not available. Due to lack of data, appropriate precautions should be taken to protect the environment.

HUMAN HEALTH

Exposure Effects

No reliable data are available regarding the acute or chronic toxicity of red phosphorus. Normal sanitary practices should be employed when handling red phosphorus to prevent dust buildup.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "COMBUSTIBLE". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow of solid powder and contain spill of material, if safe to do so. Avoid contact with solid and vapour (if ignition has occurred). Cover with inert material (sand, clay, etc.). Dampen. Keep spilled material away from combustible or reactive chemicals. Keep contaminated water, if any, from entering sewers or watercourses. Wear firefighters' full protective clothing and self-contained breathing apparatus.

Fire Control

Wear firefighters' full protective clothing and self-contained breathing apparatus. Use water spray or fog to extinguish. Cool fire-exposed containers with water. Use water or dry chemical on small fires. Move containers from fire area, if possible without risk. Do not open containers that have been heated.

COUNTERMEASURES

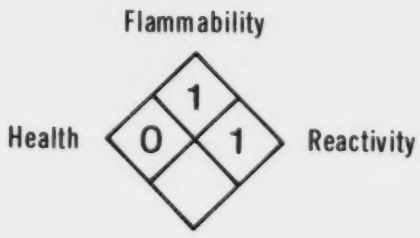
Emergency Control Procedures in/on:

Soil: Construct barriers to contain spilled solid. Remove material by manual or mechanical means taking into consideration that friction may cause ignition. Cover with inert material (sand, clay, etc.), dampen, and place in clean metal containers tightly sealed.

Water: Contain by damming, water diversion or natural barriers. Dredge or vacuum pump (suction hoses) to remove contaminated material

NAS HAZARD RATING

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

	White (Yellow) (P_4)	Red (P_x)
Appearance	Colourless or white to pale yellow solid, waxy appearance (Merck 1983)	Red to violet crystalline or red to reddish-brown amorphous powder (CRC 1983; Merck 1983)
Usual shipping state(s)	Solid packed under water	Solid
Physical state at 15°C, 1 atm	Solid	Solid
Melting point	44.1°C (Kirk-Othmer 1981)	590°C @ 4.4×10^3 kPa (Kirk-Othmer 1981)
Boiling point	280.5°C (Kirk-Othmer 1981)	(Cryst.) Ignites at 200°C (CRC 1982) (Amorph.) 260-280°C (CRC 1982; Merck 1983)
Sublimation point	20°C (3.33 Pa), 25°C (5.73 Pa), 30°C (9.60 Pa), 35°C (11.9 Pa) 40°C (16.3 Pa)	416°C (Merck 1983)
Vapour pressure	24.1 Pa (44°C) (Merck 1983)	
Light sensitivity	Darkens in sunlight (Erco 1983)	

Densities

Specific gravity	(Liq.) 1.745 @ 44.5°C (Hawley 1977) (α) 1.8232 (Bailar 1973), 1.82 (20°) (Hawley 1977, Erco 1983)	
Density	(α) 1828 kg/m^3 (Bailar 1973) (Liq.) 1740 kg/m^3 @ 50°C (Bailar 1973; Erco 1983)	(Cryst.) 2340 kg/m^3 (Bailar 1973) (Amorph.) 2160 kg/m^3 average (Bailar 1973)
Vapour density	Ignites on contact with air	Ignites in air above ~280°C
Bulk density		(Amorph.) 0.95-1.2 (Hooker MSDS 1980)

Fire Properties

	White (Yellow) (P_4)	Red (P_x)
Flammability	Ignites spontaneously on contact with air at or above 30°C (NFPA 1978); generally stored under water	Combustible solid, ignition temperature 260°C. Commercial material reacts slowly with oxygen and water vapour in air; spontaneous combustion possible in storage piles; critical thickness defined (Kirk-Othmer 1981; PB 244046)
Autoignition temperature (air)	33.9°C (Stauffer PSI) (Moist air) ~30°C, (Dry air) >30°C (Merck 1983)	260°C (NFPA 1978;
Burning characteristics	Produces voluminous amount of white P_4O_{10} smoke and considerable heat (Stauffer PSI; Merck 1983)	Produces voluminous amount of white P_4O_{10} smoke and considerable heat (Hooker MSDS 1980; Merck 1983)
Explosiveness	Explosive on contact or when mixed with some oxidizing materials (NFPA 1978; Merck 1983)	Explosive on contact or when mixed with some oxidizing materials (NFPA 1978; Merck 1983)
Behaviour in a fire	Phosphorus below its autoignition temperature exposed to air will oxidize and heat to that temperature. In a confined space, it will consume all available oxygen. See Burning characteristics (Stauffer PSI)	Heat may cause reversion to white phosphorus (CHRIS 1978; Hooker MSDS 1980). Ignites in air when heated to about 260°C (Merck 1983)
Other Properties		
Molecular weight of pure substance	123.90 (Bailar 1973)	(Amorph.) 30.97• X (Hooker MSDS 1980; Hooker DS 1980)
Constituent components of typical commercial grade	99.9 percent phosphorus (Kirk-Othmer 1983)	98 percent phosphorus, min. (Hooker DS 1980)
Resistivity	1×10^9 ohm•m (11°C) (Bailar 1973)	
Refractive index (D line)	1.8244 (29.2°C) (Bailar 1973)	

	White (Yellow) (P_4)	Red (P_x)
Viscosity	2.34 mPa•s (liquid-supercooled, 21.5°C) (CRC 1982) 0.967 mPa•s (sat. with H_2O, 50°C) (Erco 1983)	
Hardness (MOHs scale 1=talc, 15=diamond)	0.5 (CRC 1982)	
Latent heat of fusion	20.3 kJ/kg (44.1°C) (CRC 1982; Bailar 1973)	18.8 kJ/mole (597°C) (JANAF 1971)
Latent heat of sublimation	455.2 kJ/kg (25°C) (Bailar 1973) [($P_4(\alpha) \ddagger P_{4(g)}$)]	(Cryst.) 248.4 kJ/kg (597°C) (Wicks 1963)
Latent heat of vaporization	544.3 kJ/kg (287°C) (CRC 1957)	
Heat of formation	(Gas) 475.8 kJ/kg (25°C), 534.9 kJ/kg (0°C) (CRC 1982)	(Triclinic) 567.7 kJ/kg (25°C), 511.0 kJ/kg (0°C) (CRC 1982) (Amorph.) 243.3 kJ/kg (25°C) (CRC 1982) (based on P unit = 30.97)
Ionization potential	10.49 eV (as P) (CRC 1982)	
Heat capacity Constant pressure (C_p)	(α, (P)) 770.3 J/(kg•K) (25°C) (CRC 1982) (α, (P_4)) 749.5 J/(kg•K) (25°C), 768.1 J/(kg•K) (44.1°C) (Bailar 1973) (Gas, (P_4)) 542.4 J/(kg•K) (25°C) (CRC 1982; Bailar 1973)	(Triclinic) 685 J/(kg•K) (25°C) (CRC 1982)
Constant volume (C_v)	20.3 J/(mole• °C) (25°C) (JANAF 1971; Perry 1973)	18.1 J/(mole• °C) (25°C) (JANAF 1971; Perry 1973)
Thermal conductivity	(Solid, α) 0.00250 W/(cm•K) @ 0°C, 0.00236 W/(cm•K) @ 25°C (CRC 1982) (Liq.) 0.00181 W/(cm•K) @ 100°C (CRC 1982)	
Thermal expansion	3.5 percent @ 44.1°C (Erco 1983)	
Critical temperature	(Liq.) 675-695°C (Kirk-Othmer 1981; Bailar 1973)	
Critical pressure	8.12-8.33 MPa (Kirk-Othmer 1981; Bailar 1973)	
Surface tension	(Liq.) 43.09 x 10^{-3} N/m (78.3°C), 35.56 x 10^{-3} N/m (132.1°C) (Bailar 1973)	
Electronegativity	(α) 2.19 (Bailar 1973)	

	White (Yellow) (P_4)	Red (P_x)
Heat of combustion	23 999 ± 34 kJ/kg (Bailar 1973)	(Amorph.) 23 762 ± 17 kJ/kg (Bailar 1973) (Cryst.) 23 577 ± 13.5 kJ/kg (Bailar 1973)
Triple point		589.5°C @ 4.4 MPa (Merck 1983)
Solubility		
In water	Very slightly soluble (CRC 1982) (α) 3 mg/L (0.00039/100 mL) (Sullivan 1979)	Insoluble (CRC 1982; Kirk-Othmer 1981)
In other common materials	Carbon disulphide, 1250 g/L (15°C), Benzene, 28.6 g/L; Chloroform, 25 g/L; Diethyl ether, 9.8 g/L; Ethanol, 2.5 g/L (Sullivan 1979)	Amorphous red phosphorus is not soluble to any extent in any solvent with which it does not react (Kirk-Othmer 1981)
	Carbon disulphide, 1132 g/L (10°C); Soluble in PCl_3, $POCl_3$, SO_2(l), NH_3(l).	
	Slightly soluble in xylene, methyl iodide, glycerine and acetic acid (Bailar 1973) Soluble in alkali, toluene (CRC 1982)	

Vapour Weight to Volume Conversion Factor

1 ppm = 5.155 mg/m^3 (20°C) (based on P_4 unit) (Verschueren 1977)

Allotropic Forms and General Discussion of Properties

Elemental phosphorus does not occur naturally in the biosphere. It is manufactured by the reduction of phosphate rock with coke and silica, generally in an electric furnace. The elemental phosphorus produced is in the gaseous phase, and is condensed and collected under water as common white phosphorus. Phosphorus exists in several allotropic forms, namely white (yellow), red, and black. (As a general rule, commercial elemental phosphorus (P_4) is referred to as yellow phosphorus within the industry. For the purposes of this manual, it is in most cases referred to as the more

scientifically correct white phosphorus.) Because the properties of these forms are so different, the following brief explanation is presented to familiarize the reader.

The best known and commercially most important product is white phosphorus (α), sometimes referred to as yellow phosphorus. The slight yellow discoloration of commercial phosphorus supposedly results from a trace impurity, i.e., red phosphorus. Actually, the pure material is a colourless to white waxy solid that melts at 44.1°C to a clear, colourless liquid. This α-form, when cooled below -76.9°C, is converted reversibly to the β-form which has the same general appearance as its precursor. The density of the latter, 1.88 g/cm^3, is slightly higher than that of the former, 1.82 g/cm^3, which is due to its different crystal structure. The crystal structure of the α-form is cubic, with large unit cells containing 56 P_4 tetrameric molecules. This form of phosphorus is extremely reactive (and toxic), with much of this reactivity attributed to retention of the discrete tetrahedral structure in the solid, liquid and gaseous states. The material self-ignites at about 34°C and is usually stored under water. It darkens on exposure to light.

Continued heating of molten white phosphorus to temperatures above 800°C causes some dissociation to a P_2 dimer. Some monatomic phosphorus forms at 1500°C. If the α-form is heated to temperatures between 230 and 580°C for a given time (dependent upon the exact temperature), it converts to red phosphorus. Generally, red phosphorus is prepared commercially by heating white phosphorus at about 400°C for several hours. The colour of red phosphorus, generally a deep red, sometimes varies from deep maroon to orange-red and even reddish-violet. The colour varies with temperature and possibly with method of preparation. Large dark crystals become lighter when powdered. In general, colours are an indication of particle size rather than phase difference. As particle size decreases or as the temperature is lowered, colour goes from violet to red to orange. This colour change is depicted in the chart on the following page.

The physical properties of red phosphorus are variable. This probably results from the existence of a number of different polymeric modifications which may coexist in a given preparation. There are probably five or six forms of red phosphorus - two well-defined crystalline modifications, a high-temperature crystalline form, and two poorly defined crystalline modifications. X-ray diffraction studies, however, do not provide evidence for crystallinity in commercial (amorphous) red phosphorus. It has been suggested that the structure of red phosphorus may be the result of cleavage of one of the P_4 tetrahedron bonds followed by polymerization into a molecular chain of variable length and possibly different terminal groups. White phosphorus is extremely reactive; red

Temperature (°C)	Time (h)	Colour	X-ray Pattern*	Density (g/cm^3)
-	-	violet	I	2.1
400	17.5	violet-red	I	
450	20	dark red	II or III	
475	17		IV	2.30
510	4	bright orange	IV	
555	48	red	IV	2.33
560	17	red	IV	2.30
570	715	red	V	2.33
575	18		V	2.37
575	20.75		V	
595	20	red	V	2.38

* The designations under X-ray Pattern indicate a distinct pattern that can be easily distinguished from others (Stephenson 1969).

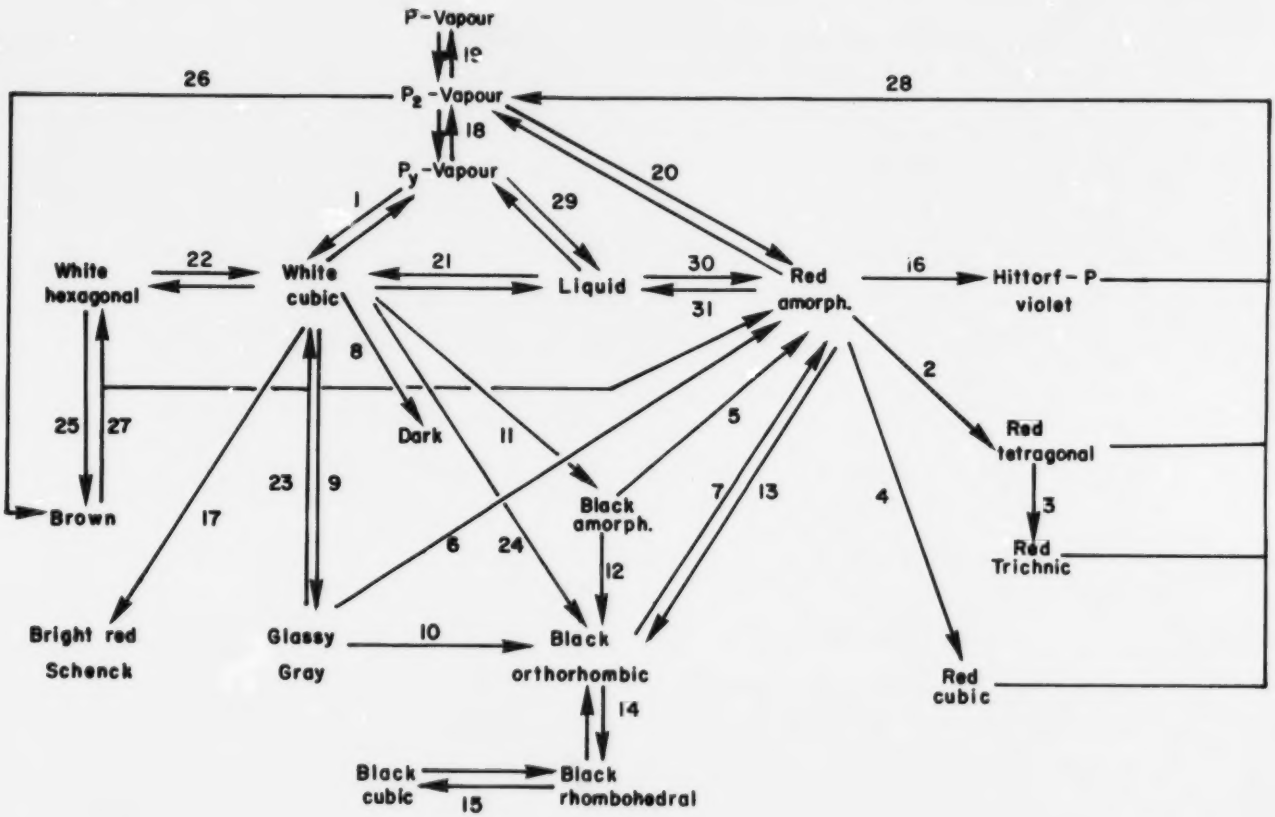
phosphorus is much less reactive, of undetermined toxicity, and easier to handle. It does, however, react very slowly with water vapour and oxygen in air under normal temperature and humidity conditions. Some references indicate red phosphorus may revert to the white allotrope with heat in air.

The final allotrope to be discussed here is black phosphorus, which is said to exist in two or four forms. Generally, the most common forms are a crystalline (orthorhombic) variety with a density of 2.69 to 2.70 g/cm^3 and a melting point around 610°C, and an amorphous variety with a density of 2.25 g/cm^3. Black phosphorus can be prepared by heating white phosphorus to temperatures of several hundred degrees Celsius while subjecting it to pressures in excess of 1.01 x 10^9 Pa (1.0 x 10^3 atm). The structure of crystalline black phosphorus consists of infinite puckered layers of phosphorus atoms configured in a zig-zag or corrugated shape. The material is superficially similar to graphite and will conduct electricity, whereas white phosphorus is a nonconductor. At temperatures greater than about 550°C, it converts to red phosphorus. Both the red and black forms are virtually insoluble in all solvents with which they do not react. The black orthorhombic form is said to be the most stable form of elemental phosphorus. It is completely stable in air and can be ignited only with difficulty. Two other crystalline forms, with densities of 3.56 and 3.83 g/cm^3, are said to exist. Other properties of black

phosphorus include ΔH_{subl} = 1307.7 kJ/kg @ 25°C (Bailar 1973), sublimation point = 490°C (N_2 atm), ΔH_f = -1207.8 kJ/kg @ 25°C, and thermal conductivity (polycrystalline) = 0.132 W/(cm•K) @ 0°C and 0.121 W/(cm•K) @ 25°C (CRC 1982). Vapour pressure = 0.133 kPa @ 290°C, 1.33 kPa @ 338°C, 5.33 kPa @ 371°C, 13.3 kPa @ 393°C, 53.3 kPa @ 432°C and 101.3 kPa @ 453°C (all solid state) (CRC 1957). In some references, the exact form of black phosphorus was not stated. In cases where conversion was made to SI units and the term "mole" was specified (and P or P_4 not indicated), the term was converted to grams by dividing by 30.97.

The same liquid is obtained from melted white, red or black phosphorus, or from condensed vapour. White phosphorus is obtained upon solidification. The liquid boils at 280.5°C, and exhibits a density of 1.74 g/cm^3 and a viscosity of 1.69 mPa•s at 50°C. The critical temperature of liquid phosphorus is 675°C (720.8; Rav 1975) and the critical pressure is 8106 kPa (10 396 kPa; Rav 1975) (Sullivan 1979; Bailar 1973; Kirk-Othmer 1981; Merck 1983; Cotton 1972). The complicated modifications of phosphorus are summarized in the diagram shown on the following page (Ullmann 1979).

White phosphorus burns in air as a solid and/or liquid, apparently without any significant quantity of unoxidized vapour appearing in the combustion cloud. The smokes from the red and white allotropes are almost identical; that from the black allotrope is presumed to be similar. The white allotrope fumes and ignites spontaneously when exposed to air; the red and black varieties are more stable. A voluminous cloud of oxides will form on ignition. (Sections 5.3.1, 7 and 7.6 present further descriptions.) The cloud is primarily phosphorus pentoxide (P_4O_{10}), with other oxides (e.g., phosphorus trioxide (P_4O_6), tetroxide (P_4O_8), and others best described as PO_x) no doubt present in varying amounts. The trioxide is formed in about 50 percent yield in a deficiency of oxygen. Other materials which do not contain phosphorus (O_3, H_2O_2) may also be formed during combustion due to the presence of moisture. Phosphine (PH_3) may be present if caustics are involved. The combustion process will rapidly deplete a closed volume of life-supporting oxygen. The oxides have a strong affinity for water and will extract moisture from the atmosphere; the pentoxide is considered to be one of the most effective drying agents at temperatures below 100°C. The oxyacids, e.g., phosphoric acid (H_3PO_4), and their hydrolysis precursors will also be present in the combustion cloud. The complete chemistry of phosphorus oxides and their reactions with water are complicated and cannot be explained in this brief discussion. The reader is advised to review the



1. High vapour pressure at room temperature
2. Conversion about 540°C
3. About 550°C
4. About 600°C
5. About 125°C
6. About 400°C
7. About 550°C
8. About 300°C and 8.0 x 10^5 kPa
9. Heat to 380°C with mercury or to over 250°C at 1.2 x 10^6 kPa
10. Heat to 400°C with mercury
11. Conversion about 200°C and 1.2 x 10^6 kPa
12. About 200°C and 1.5 x 10^6 kPa
13. About 200°C and 1.2 x 10^6 kPa
14. About 5.0 x 10^6 to 1.0 x 10^7 kPa
15. About 1.10 x 10^7 kPa
16. Recrystallize from melted lead
17. As a precipitate from a PBr_3 solution
18. Conversion about 900°C
19. About 1700°C
20. At low pressure
21. At 44.1°C (can supercool)
22. At -77°C or at 64°C and 1.2 x 10^5 kPa
23. Sublimes under vacuum
24. Conversion about 220°C and 1.2 x 10^6 kPa
25. UV irradiation at -190°C
26. Condensation from P_2 vapour at -196°C
27. Warm over -100°C
28. Heat at low pressure
29. Boiling point 280°C
30. Heat at 300°C or influence of light or X-rays
31. Melting point approx. 600°C

specific references (Sullivan 1979; Bailar 1973; Kirk-Othmer 1981; Merck 1983; Cotton 1972; Stephenson 1969; Ullmann 1979; Steubing 1980). It is also to be pointed out that phosphorus, P_4, will react with water at temperatures above 280°C to give phosphorous acid (H_3PO_3) and phosphine (PH_3) (Van Wazer 1958).

One of the most important reactions of phosphorus is that of oxidation by oxygen; as such, the process has been extensively studied and has resulted in the theory of branching-chain reactions. On the basis of this theory, it is predicted there are upper and lower critical pressures of oxygen for a given pressure of phosphorus. Ignition of the vapour occurs between these critical pressures; outside of this range of oxygen pressures, the rate of oxidation is very slow. To a first approximation, the lower critical pressure, $P_{O_2}{}^L$, is inversely proportional to the pressure, P_{P_4}, of phosphorus vapour and the square of the diameter of the containing vessel. The lower critical pressure is also lowered by the addition of inert gases and is independent of temperature. This relationship is shown by the following equation:

$$P_{O_2}{}^L P_{P_4}\left[1 + \frac{uP_x}{P_{O_2}{}^L + P_{P_4}}\right] d^2 = K_L$$

where K_L is a constant, P_x is the pressure of the inert gas, and u is a factor depending on the coefficient of diffusion of oxygen in the added inert gas (u = 0.13 for He and 0.84 for CCl_4; no value for N_2 was given). The upper critical pressure, $P_{O_2}{}^U$, of oxygen is proportional to the pressure of phosphorus vapour according to:

$$P_{O_2}{}^U/P_{P_4} = K_u C^{E_1/RT}$$

The value of E_1 is less than 4186.8 J. $P_{O_2}{}^U$ decreases slightly as the temperature increases and is only slightly affected by the presence of an inert gas. The theoretical relationship between the upper and lower critical pressures of oxygen and phosphorus vapour without the pressure of an inert gas is shown in Figure 1. The experimental values agree closely with the theoretical curve except in the vicinity of the minimum, where the log P_{P_4} values fall below the curve to as low as -4.

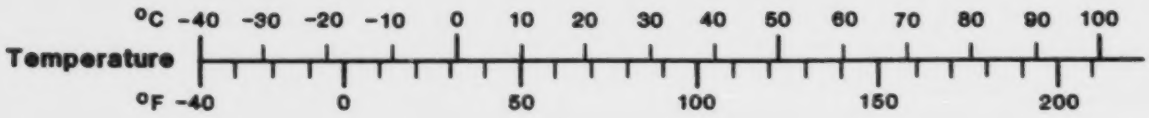
The main purpose for including the above discussion in this manual is to point out that unoxidized phosphorus vapour may exist for some finite time in air. This can present a potential toxicity problem not only for emergency response and cleanup personnel, but also for the person working with white phosphorus on a routine basis (Van Wazer 1958).

It has also been demonstrated that definite upper and lower atmospheric pressure limits exist above or below which the oxidation reaction involving white phosphorus, which is accompanied by a flame, does not proceed at all. These limits are similar to the critical pressures described above for the oxidation of phosphorus vapour. This flame reaction/glow region/no reaction scheme is shown graphically in Figure 2.

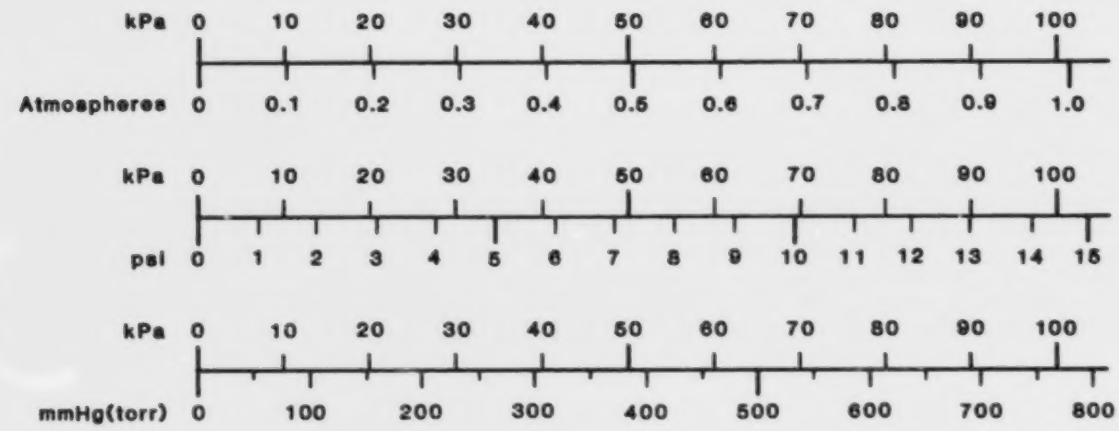
The cold oxidation (glow region) of white phosphorus has been extensively studied. The spectrum of the glow shows a continuum in the visible region and a series of bands and lines stretching from 3418 to 2371 Å. The same spectrum is produced when phosphorus trioxide (P_4O_6) burns in moist air. It is concluded that the same excited constituents must be present in both cool flames. The reader is reminded that white phosphorus usually oxidizes very rapidly and burns with a bright yellow flame which may extend for a considerable distance from the phosphorus surface, with the main product being phosphorus pentoxide under most conditions. However, other oxides are possible under proper conditions (Van Wazer 1958). It is to be concluded from the above that under the right conditions, white phosphorus can be spilled and ignition with associated flame may not occur. One may encounter a very slow reaction with glowing and some fuming, or no reaction at all.

PHOSPHORUS

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



Viscosity

Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J

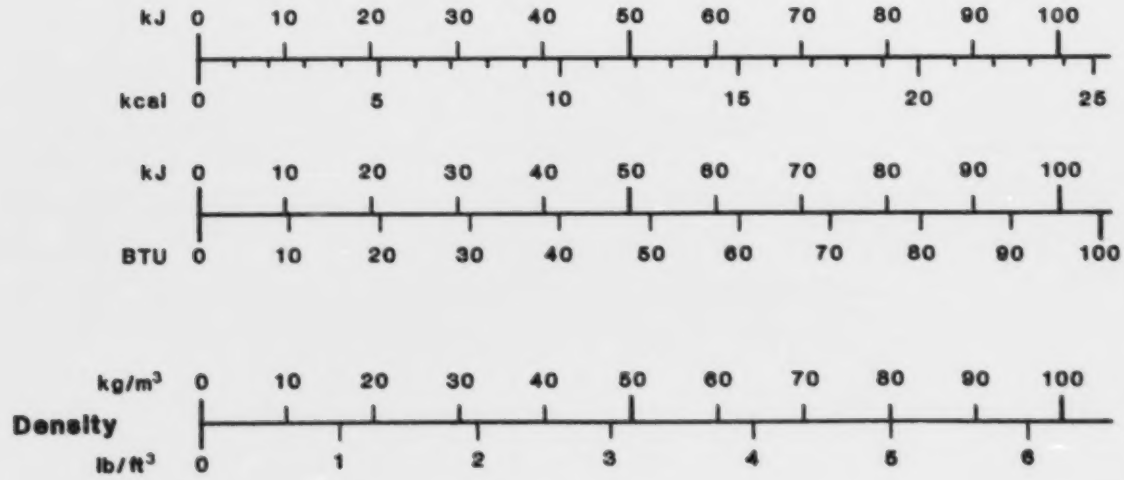


FIGURE 1

PHOSPHORUS (white)

CRITICAL PRESSURES FOR OXIDATION

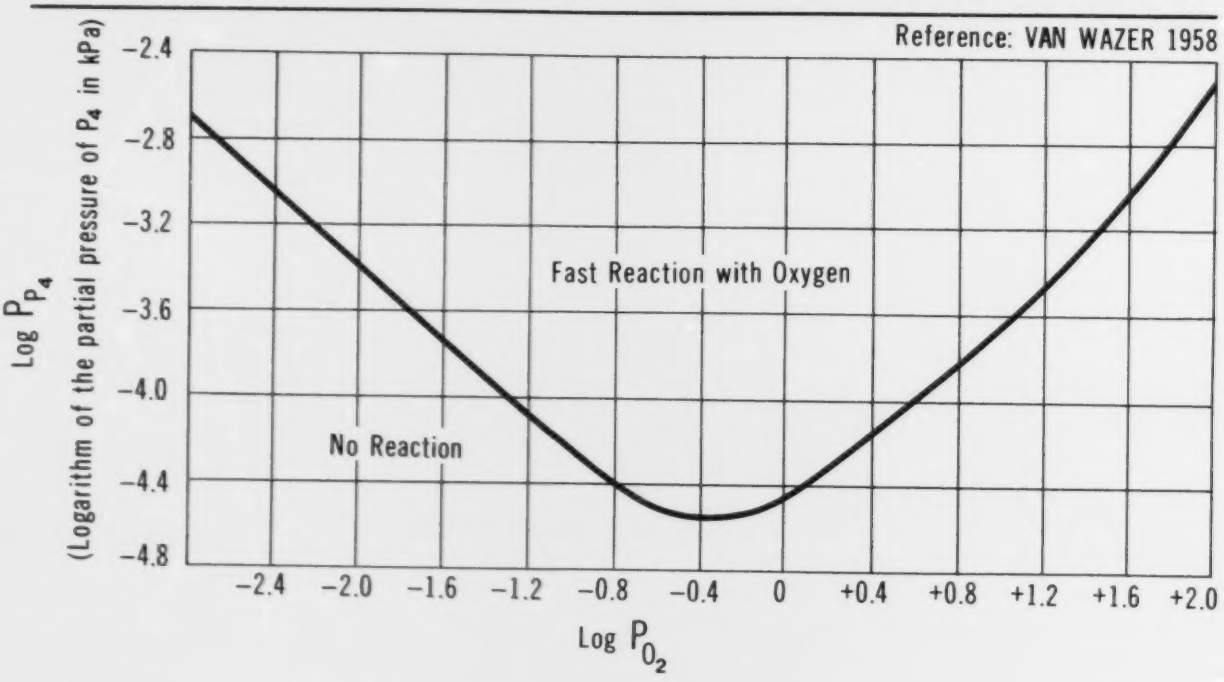


FIGURE 2

PHOSPHORUS (white)

OXIDATION LIMITS IN DRY AIR

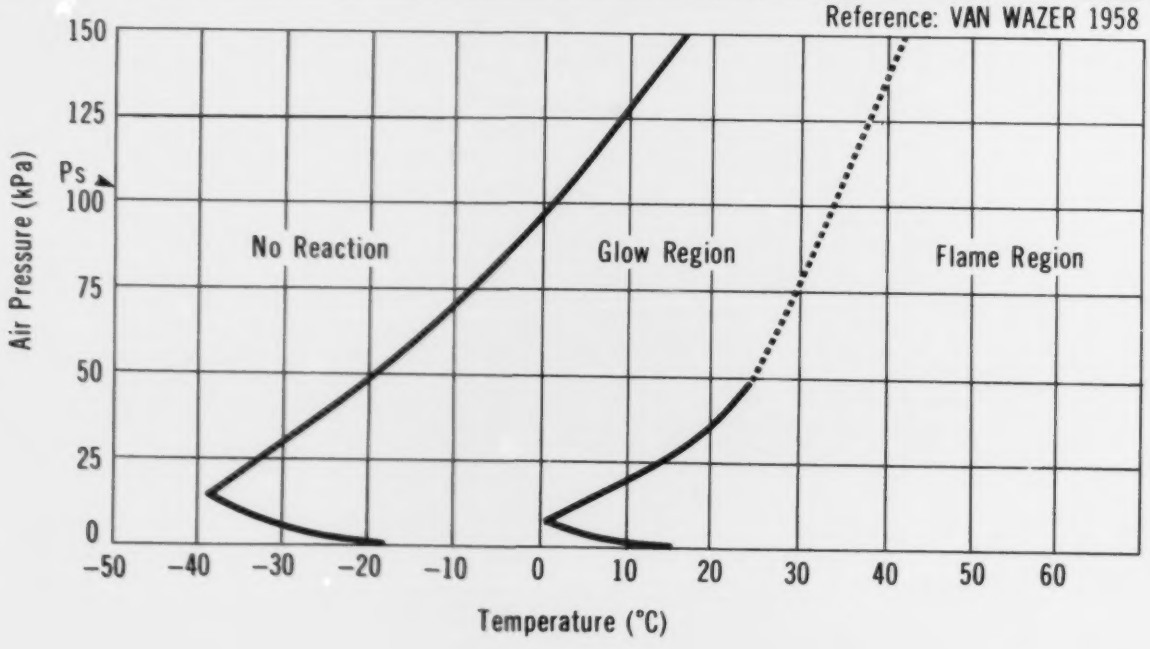


FIGURE 3

PHOSPHORUS

VAPOUR PRESSURE

Reference: KIRK-OTHMER 1982; CRC 1982; VAN WAZER 1958

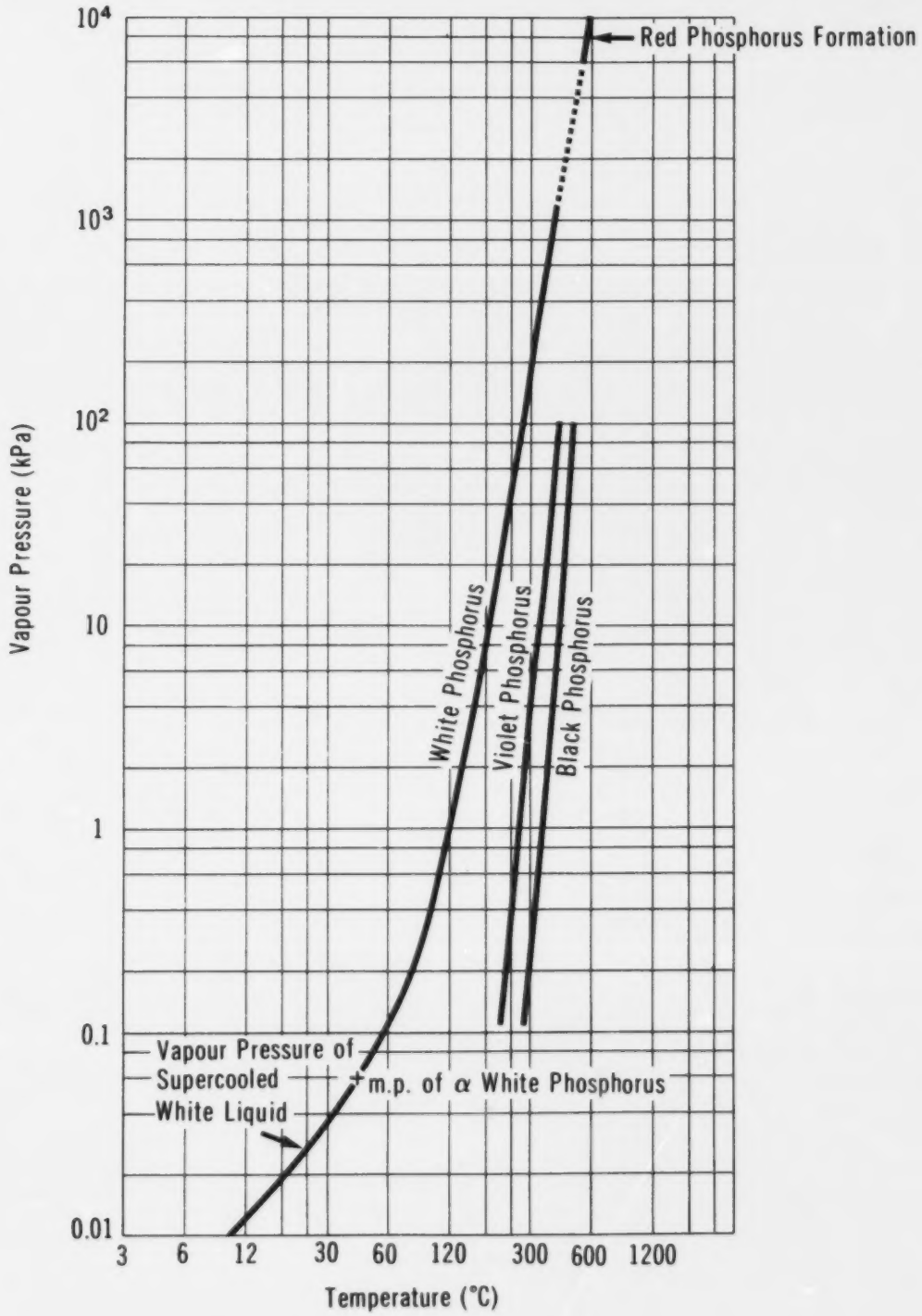


FIGURE 4

PHOSPHORUS (white, liquid)

LIQUID VISCOSITY

Reference: CRC 1982

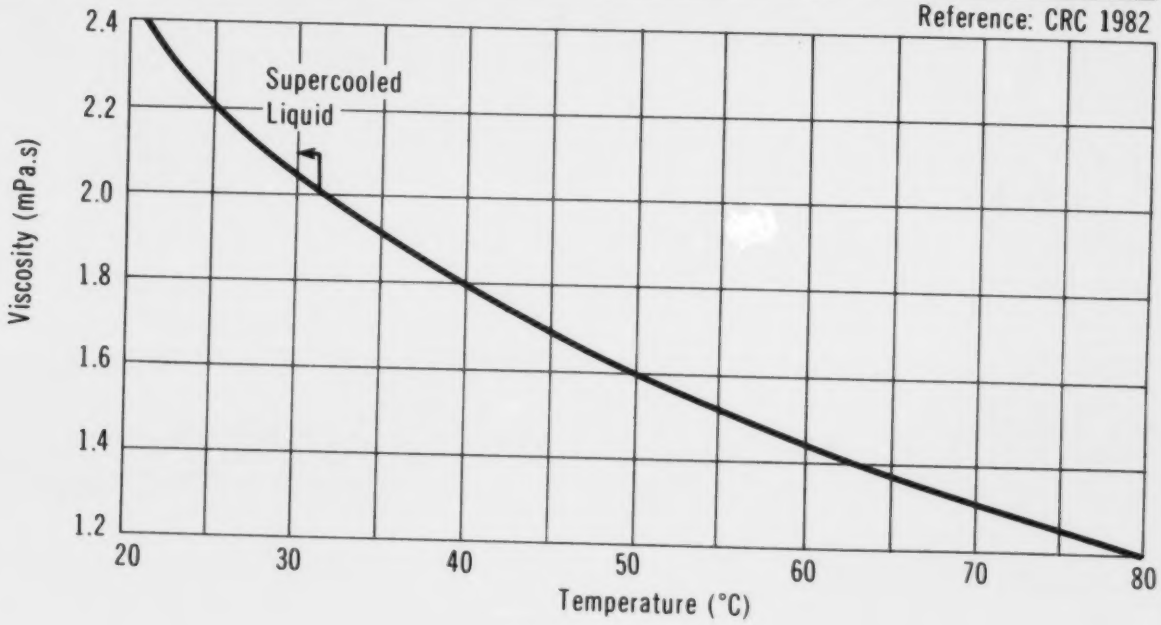
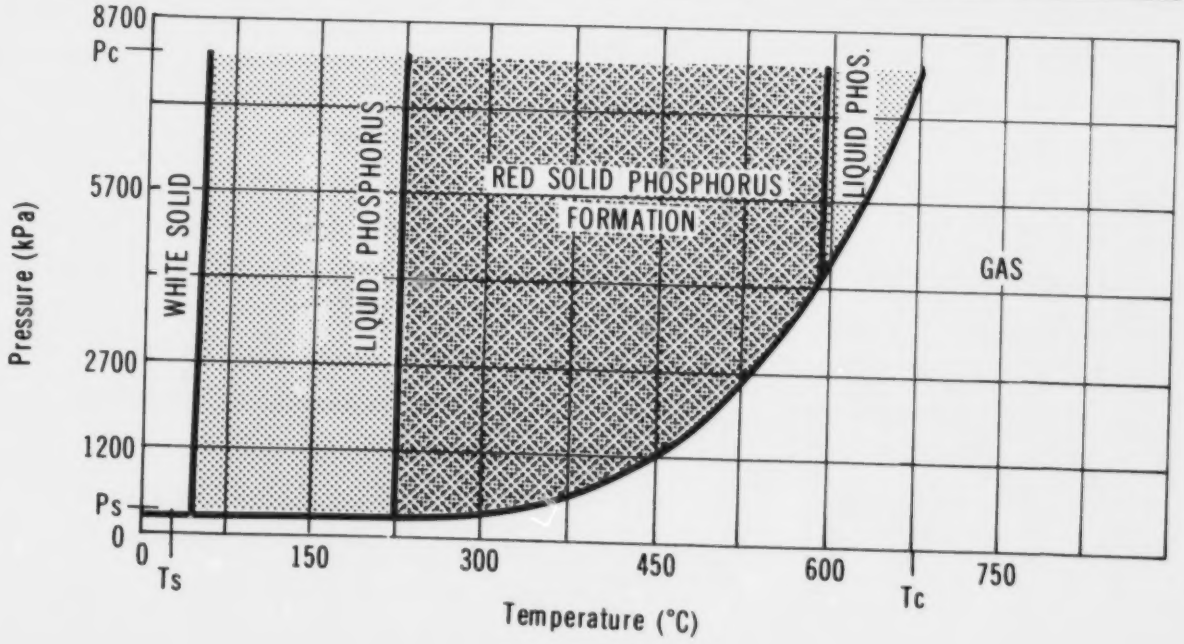


FIGURE 5

PHOSPHORUS

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Gillelan 1983)

Both white and red (amorphous) phosphorus are prepared and sold in Canada and offshore. The former is 99.9 percent pure and the latter not less than 98 percent pure.

3.2 Domestic Manufacturer (Corpus 1982; CBG 1980)

This is the corporate headquarters' address and is not intended as a spill response contact.

Erco Industries Ltd.
2 Gibbs Road
Islington, Ontario
M9B 1R1
(416) 239-7111

3.3 Other Suppliers (CBG 1980)

C-I-L Inc.
45 Sheppard Avenue East
Willowdale, Ontario
M2N 5S8
(416) 226-7532

Monsanto Canada Ltd.
2000 Argentia Road
Plaza Two, Third Floor
P.O. Box 787
Mississauga, Ontario
L5M 2G4
(416) 826-9222

3.4 Major Transportation Routes (Corpus 1982; CMI 1980; Erco 1983a)

Current Canadian production of white phosphorus is located at Long Harbour, Newfoundland, and at Varennes, Quebec. The phosphorus produced at the former plant is primarily for export, and that at the latter for shipment to plants located at Buckingham, Quebec, and Port Maitland, Ontario. Shipment is by rail and tank motor vehicles. The exported white phosphorus is mainly sent to the United Kingdom via ships fitted with hot water jacketed tanks in which the product is transported under water.

3.5 Production Levels (Corpus 1982; CMI 1980)

Company, Plant Location		Nameplate Capacity kilotonnes/year (1981)	Effective Capacity kilotonnes/year (1981)
Erco Industries, Long Harbour, Nfld.		65	45 - 55
Erco Industries, Varennes, Que.		25	10
	TOTAL	90	55 - 65
Domestic Production (1981)		55	
Imports (1981)		1.5	
	TOTAL	56.5	

3.6 Manufacture of Phosphorus (Riegels 1974; FKC 1975)

White phosphorus is produced by the reduction of phosphate rock mixed with coke and silica, the latter acting as a flux for the calcium present in the rock. The reaction takes place in an electric furnace. A modern electric furnace process for the production of white phosphorus consists of a sequence of four operations: (1) preparing the furnace burden (feed), (2) charging and operating the furnace, (3) collecting the liquid products, and (4) collecting the gaseous products. Generally, the burden must be adequately porous so the gases can escape from the reaction zone near the bottom of the furnace. The feed phosphate is therefore agglomerated/crushed to a nominal particle size range, usually 0.5-5 cm diameter, and mixed with silica and coke of similar particle size range. Sintering is an accepted method of agglomeration.

Some furnaces consist of a water-cooled, welded steel sheet shell with a floor made of carbon blocks and walls of firebrick or cast refractory cement. Most furnace roofs are cast monolithic structures. The baked-carbon electrodes enter the furnace through the roof. A control mechanism allows the electrodes to move up and down so as to keep the current constant. The raw materials (furnace charge) are distributed evenly throughout the furnace and heated electrically until the reaction occurs; elemental phosphorus (P_4) is emitted as vapour along with carbon monoxide (CO) and some silicon tetrafluoride (SiF_4). An approximate equation for the overall process is shown below. Silicon tetrafluoride, if any, is formed from the slag:

$$4Ca_5F(PO_4)_3 + 18\,SiO_2 + 30C \rightarrow 18(CaO{\cdot}SiO_2{\cdot}\,1/9\,CaF_2) + 30\,CO\uparrow + 3P_4\uparrow$$

Phosphate Rock Silica Coke Slag

Dust contained in the hot gas emission from the furnace is removed generally by precipitators. Phosphorus vapour is sometimes condensed in towers equipped with water sprays, further purified, and pumped into storage tanks. The other gaseous products of the reaction are carbon monoxide (CO) and some silicon tetrafluoride (SiF_4). The former can be burned and used as an energy source for preheating the phosphate rock prior to reduction. The latter is hydrolyzed to silicic acid (H_2SiO_3) and hydrogen fluoride (HF) in the cooling tower and ultimately to a mixture of fluorosilicates. The cooling tower water is reused until it becomes saturated with the latter. Since the water contains a small amount of dissolved/particulate phosphorus (phossy water), it cannot be disposed of to the environment without being properly treated.

Other by-products of the reduction reaction are the calcium silicate slag and ferrophosphorus. The latter is formed by reduction of the iron compounds present in the phosphate rock, silica and coke. The material contains 20-30 percent by weight phosphorus and is used in the manufacture of high strength, low alloy steels. The former by-product at one time was used as an agricultural agent or rail- or roadbed fill, blown into slag wool, or made into other slag by-products. Today, however, this use has declined because of the presence of small amounts of uranium and its daughter products originally present in the phosphate rock (Kirk-Othmer 1981; CMI 1980).

Red phosphorus is usually manufactured by a batch process, although continuous methods have been developed. The white allotrope is converted to the red in a steel or cast-iron vessel which generally contains about 1000 kg of material. Liquid phosphorus protected by a layer of water is passed into the vessel which is then sealed. Heat is applied gradually so the unconverted liquid does not boil violently or the mass bump. The vessel is equipped with a reflux condenser to retain the liquid.

The mass remains fluid until approximately half of the liquid has been converted to the red allotrope. The mass continues to thicken until solidification occurs when the red phosphorus content is about 70 percent by weight. The conversion process is exothermic; the heat input must therefore be carefully controlled to prevent a rapid increase in the reaction rate and accompanying mass eruption. The potential for the latter is high while the mass is in the semirigid state. The final heating is at about 400°C for several hours.

The mass is then allowed to cool. The red phosphorus is chipped from the mass and removed while immersed in water. Immersion is necessary because traces of unconverted white allotrope are mixed in with the red and ignition may occur if air is

contacted. The material is therefore wet-ground and boiled with sodium carbonate (Na_2CO_3) solution which effectively removes the white modification. The product is then sieved, washed on a rotary filter, and vacuum dried. Other processes, such as heated ball mills, as well as one involving a heated screw, have been used as converters. These latter methods eliminate the need for chipping the red phosphorus from the reaction vessel. The red phosphorus product can be stabilized by 1) suspending the material in a 1 percent by weight solution of sodium aluminate ($Na_2Al_2O_4$) then aerating the resulting slurry for several hours, and 2) precipitating magnesium oxide (MgO) onto the red phosphorus in a ratio of about one part to a hundred parts of the phosphorus (Kirk-Othmer 1981).

3.7 **Major Uses in Canada** (Corpus 1982; CMI 1980)

Of the total amount of white phosphorus produced and imported in 1981 (56.5 kt), 34.5 percent was consumed domestically and 65.5 percent was exported. The total domestic demand in 1981 was 19.5 kt, of which 95 percent was used to produce both technical and food grade phosphoric acid (H_3PO_4), 3 percent was used to produce red phosphorus (P_x), 0.5 percent was used to produce phosphorus sesquisulphide (P_4S_3), 1 percent was used to produce phosphine (PH_3) and 0.5 percent was used in the manufacture of miscellaneous products.

3.8 **Major Buyers in Canada** (Corpus 1982)

The major buyers of phosphorus in Canada are Canada Metals, in Toronto, Ontario, which manufactures phosphorus bronzes, and Cyanamid Canada, in Niagara Falls, Ontario, which manufactures phosphine.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. White phosphorus is transported in the liquid state under a water cover in railway tank cars and tank motor vehicles. In some instances, it is transported in 0.114 m^3 (25 gal.) steel drums in railway freight cars.

4.1.1.1 Railway tank cars. Railway tank cars used for the transportation of liquid white phosphorus are classified under CTC/DOT regulations and conform to CTC/DOT Specifications 103W, 111A60F1 or 111A60W1. Table 2 describes the railway tank cars under these classifications. The tank car in predominant use is considered to be 111A60W1 (CTC 1974; Erco 1983).

TABLE 2 RAILWAY TANK CAR DETAILS

CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
103W	Steel fusion-welded tank with dome. Uninsulated or insulated. General service. 2% dome. Safety valves (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Bottom outlet or washout optional.

* Canadian Transport Commission and Department of Transportation (U.S.)

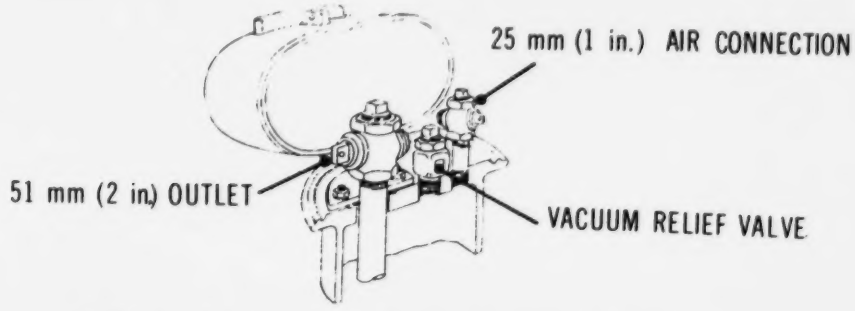
The capacity of the 111A60W1 tank car varies from 75 700 to 90 900 L. A typical 111A60W1 tank car is depicted in Figure 6; Table 3 indicates the specifications associated with this drawing. The cars are equipped with approved dome fittings, external heater systems, and insulation at least 10 cm (4 in.) thick (the insulation thickness may be reduced to 5 cm (2 in.) over external heater coils). The tank cars are not equipped with a

FIGURE 6

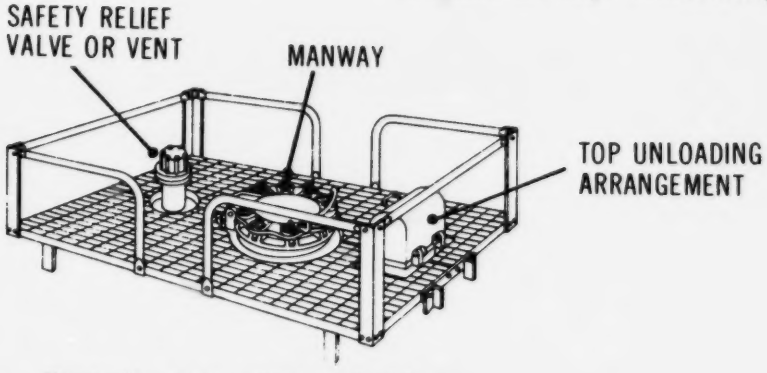
PHOSPHORUS

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979; CTC 1974)



Detail of top unloading arrangement



Detail of loading platform

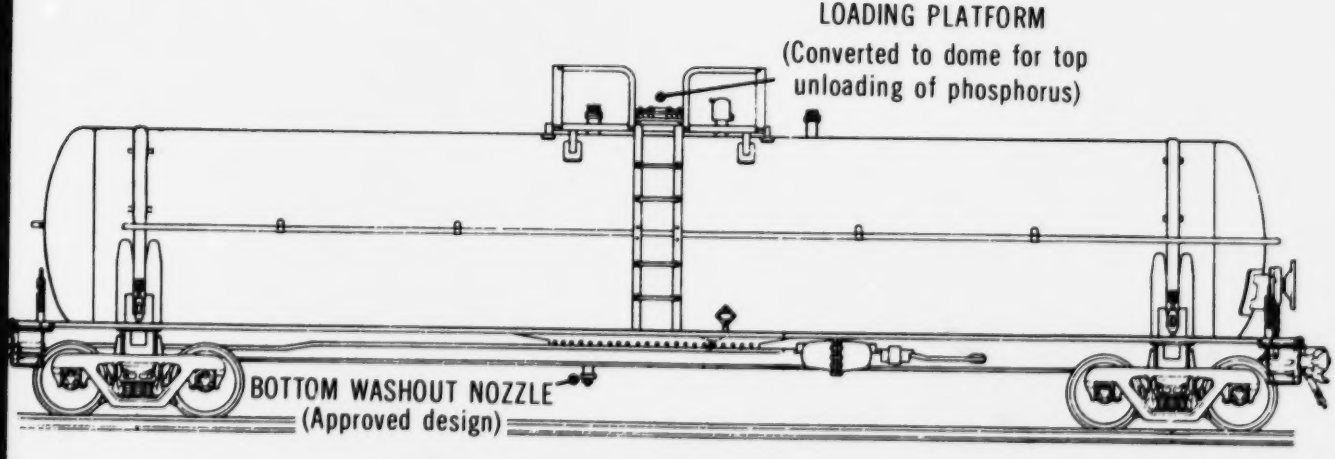


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; CTC 1974)

Description	Tank Car Size (Imp. gal.)					
	16 700		17 200		20 000	
Overall						
Nominal capacity	75 700 L	(16 700 gal.)	78 000 L	(17 200 gal.)	90 900 L	(20 000 gal.)
Car weight - empty	33 900 kg	(74 700 lb.)	33 900 kg	(74 700 lb.)	38 900 kg	(85 800 lb.)
Car weight - (max.)	119 000 kg	(263 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
Tank						
Material	Steel		Steel		Steel	
Thickness	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)
Inside diameter	2.60 m	(102 in.)	2.62 m	(103 in.)	2.74 m	(108 in.)
Test pressure	414 kPa	(60 psi)	414 kPa	(60 psi)	414 kPa	(60 psi)
Burst pressure	1640 kPa	(240 psi)	1640 kPa	(240 psi)	1640 kPa	(240 psi)
Approximate Dimensions						
Coupled length	17 m	(57 ft.)	17 m	(57 ft.)	18 m	(60 ft.)
Length over strikers	16 m	(53 ft.)	16 m	(53 ft.)	17 m	(57 ft.)
Length of truck centers	13 m	(42 ft.)	13 m	(42 ft.)	14 m	(45 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(13 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width (over grabs)	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)
Width of grating	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)
Loading/Unloading Fixtures						
Top Unloading						
Unloading connection	51 mm	(2 in.)	51 mm	(2 in.)	51 mm	(2 in.)
Manway/fill hole	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)
Air connection	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)
Bottom Unloading[1]						
Bottom outlet	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)
Safety Devices	Safety vent (frangible disc) or valve					
Dome	Dome equipped for top unloading of phosphorus					
Insulation	Minimum 51 mm (2 in.) in thickness over external heater coils					

1 Railway tank cars are not equipped with bottom outlets for unloading phosphorus; however, bottom washout nozzles may be applied. The latter must be of approved design.

bottom outlet for discharge; however, bottom washout nozzles of approved design may be applied. The liquid phosphorus must be blanketed with an inert gas or immersed in water, with the water level reaching into the dome, but not exceeding more than 50 percent of the capacity of the dome. The temperature of the phosphorus during the loading process must not exceed 60°C (CTC 1974).

Liquid phosphorus is loaded and unloaded from the top of the tank car through a closed circuit system. The tank car is initially filled with water. Prior to loading, the water is heated to a temperature not exceeding 60°C and is then displaced by the liquid phosphorus. During the unloading process, this procedure is reversed, namely, the liquid phosphorus is displaced by heated water. In all cases, whether the tank car contains liquid phosphorus plus water or just water, the water level must extend into the dome but not exceed 50 percent of the capacity of the dome. The ullage contains air in either case. A water-filled tank car must be placarded with "EMPTY - VIDE, SPONTANEOUSLY COMBUSTIBLE" before the car is offered for return movement (Erco 1983; CTC 1974).

4.1.1.2 Tank motor vehicles. The transportation of liquid white phosphorus by tank motor vehicles is not at present regulated in Canada, but Erco voluntarily applies the rail regulations, insofar as appropriate, to such shipments and is guided in the specifications of the tank motor vehicles by TC/DOT Specifications MC 310, 311 or 312 (See Table 4 for details). Loading and unloading procedures are similar to those for railway tank cars (Erco 1983).

TABLE 4 TANK MOTOR VEHICLE DETAILS

TC* Specification Number	Description
TC 312	Steel butt-welded tank. Design and construct in accordance with ASME Code when unloading by pressure in excess of 103 kPa (15 psi). Gauging device not required. Top and/or bottom discharge outlet. Minimum one pressure relief device per compartment. One minimum 380 mm diameter manhole per compartment. Bottom washout optional.

* Transport Canada

4.1.2 Non-bulk Containers. White phosphorus, dry or under water, is also transported by rail freight in authorized non-bulk containers as specified in CTC (1974). When packed under water, the containers must meet Specifications 5A, 6A, 6B (metal barrels or drums not over 0.114 m^3 (25 gal.) capacity each) or 15A, 15B (wooden boxes with inside containers, which must be hermetically sealed (soldered) metal cans, enclosed in other hermetically sealed (soldered) metal cans). Other details exist for the latter two specifications. During the loading procedure, the non-bulk container is submerged in water heated to a temperature not exceeding 60°C and filled to a specified level with liquid phosphorus. Sufficient water is left over the liquid to provide a water cover after the phosphorus has solidified. Some contraction, accompanied by shrinking from the metal interface, occurs during the cooling process.

White phosphorus, if to be transported dry, must be cast solid and shipped in containers conforming to Specifications 6A, 6B or 6C (metal barrels or drums not over 0.114 m^3 (25 gal.) capacity each). White phosphorus transported by rail express must be packed under water in containers conforming to Specifications 15A or 15B (wooden boxes with inside containers which must be hermetically sealed (soldered) metal cans, containing not over 1 lb. each, enclosed in other watertight, metal cans with screw-top or soldered closures). Other details for these specifications are listed.

Red (amorphous) phosphorus is transported in steel barrels or drums conforming to Specifications 6A or 6B (also 37A or 37B), single-trip containers, for gross weight not exceeding 72.57 kg (160 lb.). Wooden boxes with metal inside containers meeting Specifications 15A or 15B can also be used. These containers are sealed air-tight and positively fastened (CTC 1974). The gross weight generally varies from 72.57 to 217.7 kg (160 to 480 lb.) (CTC 1974) (Specification 6B). The material is packed dry (Gillelan 1983). Containers approved for the transport of phosphorus are listed in Table 5. The most common net mass transported in drums is 45.4 kg, with 4.5 kg being the container weight in such cases. Elemental phosphorus is usually transported in drums with capacities of 114 L (182 kg net mass) or 210 L (334 kg net mass) (Stauffer MSDS 1980).

TABLE 5 DRUMS APPROVED FOR PHOSPHORUS BY TRANSPORT CANADA[1]

Type of Barrel or Drum	Designation	Description	Figure No.
Red (Amorphous) Phosphorus			
Steel, low carbon, open-hearth or electric	6A 6B	Removable head, closure must be of screw-thread type or secured by positive fastening	
Wooden boxes, nailed	15A 15B	Equipped with inside metal containers which are tightly and securely closed	
Steel, sheets for body and heads to be hot-rolled or cold-rolled, low carbon, open-hearth or electric	37A 37B	Single trip containers, removable head required	
White Phosphorus			
Steel, low carbon, open-hearth or electric	5A	Removable head not authorized; not over 0.114 m^3 (25 gal.) capacity; body seams welded, head and chime seams welded or double-seamed; flanges for closures welded in place; closure adequate to prevent leakage, gasket required, must be screw-thread type or fastened by screw-thread device	7
	6A 6B 6C	Removable head; not over 0.114 m^3 (25 gal.) capacity; closure adequate to prevent leakage; gaskets required, must be screw-thread type or secured by positive fastening	
Wooden boxes, nailed	15A 15B	Equipped with inside containers which are hermetically sealed (soldered) metal cans enclosed in other hermetically sealed (soldered) metal cans	

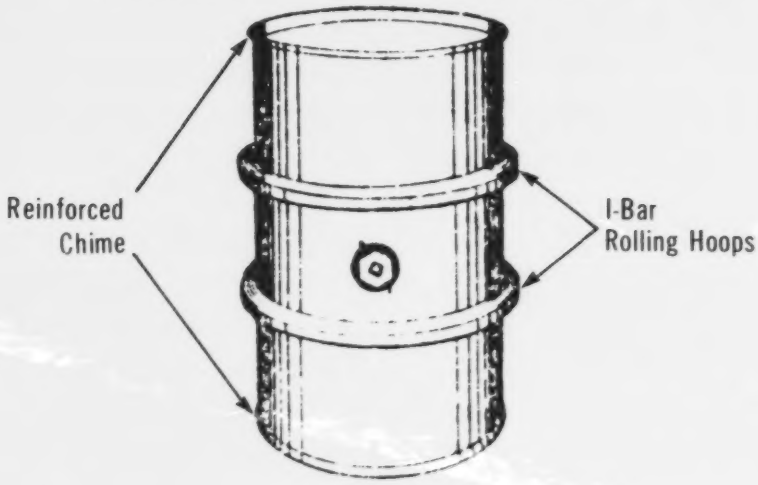
1 See CTC (1974) for designations for white phosphorus shipped dry and by rail express.

FIGURE 7

PHOSPHORUS

TYPICAL DRUM CONTAINER

Typical steel drum for white phosphorus



DOT-5A Drums

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Since phosphorus is handled in the liquid state during loading and off-loading procedures, it is recommended that handling systems be designed to maintain its temperature in the 50 to 60°C range.

Prior to off-loading, certain precautions must be taken; these are listed below (Erco 1983; MCA 1976):

- Off-loading operations must be conducted by fully trained personnel under diligent supervision (CTC 1974).
- For night-time unloading, lights must have on explosion-proof rating.
- Off-loading stations must be equipped with emergency showers or tubs of water for emergency immersion of personnel who may come in contact with white phosphorus.
- Tank car should be spotted accurately on level track.
- Brakes must be set and standard chocks or rail clamps installed (CTC 1974).
- Derails must be placed on the unloading track approximately one car length from the car being unloaded, unless the car is protected by a closed and locked switch or gate.

- Off-loading should be accomplished in limited personnel access areas and posted "Authorized Personnel Only".
- Caution signs reading "STOP - Tank Car Connected" or "STOP - Men at Work" must be placed on the track or car (CTC 1974).
- Tools used during the unloading procedure must be nonsparking.
- Personnel engaged in off-loading must wear full protective clothing and have self-contained breathing apparatus available for emergency use.
- A safe operating platform should be provided at the unloading point.

Proceed with off-loading as follows:

- Ascertain that any pressure buildup within the tank has been released and the phosphorus is completely molten (hook up external heating system if required).
- Connect the heated unloading line to the top discharge outlet.
- Connect the discharge line to the closed circuit unloading system and commence unloading.

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles. The general procedures for unloading phosphorus tank motor vehicles are similar to those for railway tank cars.

- Wheels must be chocked and a jack stand utilized for trailer support if the tractor is removed.
- External heating system should be activated prior to off-loading to ensure all phosphorus is in the liquid state.

4.2.3 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in white phosphorus service. It is recognized that other materials may be used for particular applications. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

Pipes and fittings used in liquid phosphorus service should be 316 L stainless steel. The piping systems should be heated by means of an external carbon steel hot water jacket. Other external heating systems such as electric/steam tracing can be used, but must be designed to avoid overheating of the phosphorus. Piping systems should be self-draining back into the phosphorus holding tank; provision should be made for hot water flushing before and after phosphorus transfer. Provision for expansion of the piping systems should be allowed. Handling systems should be insulated and the insulation finished with a light gauge metal covering to further minimize operator exposure to phosphorus leakage (Erco 1983).

Joints in the piping system should be welded or flanged. Gaskets can be rubberized asbestos, rubber, or other suitable material. Also, it is recommended that flanged joints be enclosed with a metal flange guard to protect operators in the event of gasket failure (Erco 1983).

Flanged ball valves ("firesafe" type) of 316 stainless steel construction with Teflon seats are recommended exclusively (Erco 1983).

Both centrifugal and positive displacement pumps are suitable for handling liquid phosphorus. The former should be fitted with double mechanical seals flushed and pressurized with hot, clean water. The latter should be fitted with suitable devices to limit pressure buildup (Erco 1983).

Storage tanks for white phosphorus should be constructed of concrete or carbon steel and should be vented to the atmosphere. All nozzles must be above the highest phosphorus level. The phosphorus is covered with water and the system should be designed so the water level remains constant. The water cover can become acidic; a minimum pH of 5.5 should be maintained. Carbon steel tanks should be provided with a stainless steel band at the water/air interface to avoid corrosion at this point. Tanks should be equipped with heating coils using either hot water or steam. They should be installed in a retaining basin constructed of concrete or welded carbon steel; the basin should be large enough to retain the full contents of the tank or tanks plus an allowance for water cover, and should not have bottom or side outlets. Adequate provision should be made for flooding the basin in the event of a phosphorus leakage (Erco 1983).

Since only 316 stainless steel, carbon steel (Schedule 80) and concrete are recommended for use with liquid white phosphorus, no table listing materials of construction is included in this manual.

5 CONTAMINANT TRANSPORT

5.1 General Summary

White phosphorus is transported in the liquid state by railway tank car and highway tanker truck, and in 0.114 m^3 (25 gal.) steel drums in railway freight cars. The large tank (railway or highway) is filled with hot water which is displaced by liquid phosphorus via a closed-circuit system. The tank is equipped with steam lines and insulated, but is not heated during transport. Since white phosphorus has a relatively low thermal conductivity, it is a good self-insulator and remains mostly liquid during transport. Some solid crust will be formed at the metal and water interfaces, especially during the winter months. It has been confirmed, however, that during the unloading procedure the phosphorus is displaced with hot water; this is generally accompanied by steam heating only in the winter months. This indicates solidification usually is not significant during transportation of white phosphorus in Canada. The white phosphorus content is covered with water; air remains in the ullage. Similarly, white phosphorus may also be loaded under hot water into steel drums of 0.114 m^3 capacity. The phosphorus is covered with water; air remains in the ullage. The extent of solidification in the drum will depend on the external temperature and the duration of the shipment; solidification is generally expected to be significant.

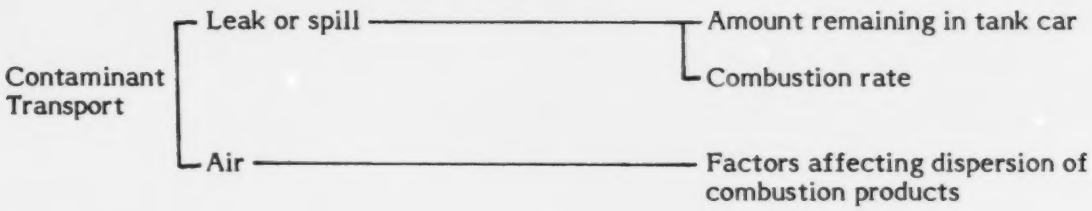
Red phosphorus, on the other hand, is transported in the dry state in steel drums and sometimes in small steel cans contained in wooden crates. An accident involving the release of significant amounts of red phosphorus is not very probable. However, due to the uncertainty of its toxicity to humans and the environment, it should still be considered potentially dangerous and possibly damaging to the environment. Ignition of the material is possible and presents the same problems associated with the combustion of the white allotrope.

If liquid white phosphorus is spilled into water, it will sink and solidify. Ignition which may occur between the release point and the water surface will be extinguished. If spilled onto soil or ice, the material will flow to some extent and solidify. Since the white allotrope ignites spontaneously in air, a spill onto a solid surface will be accompanied by ignition which may be self-sustaining even in the cold. It is conceivable that the combustion process resulting from a smaller spill may not be self-sustaining in extreme cold and especially when the material is spilled onto ice.

Transport of liquid phosphorus toward the water table, although an environmental concern due to the toxicity of the white allotrope, is highly improbable. The transport of small amounts dissolved in water or in some other chemical in which it is soluble and which may have also been spilled is possible. The water could result from precipitation or from firefighting procedures. The potential for groundwater contamination is thought to be quite low as compared to the potential for surface water contamination due to runoff or direct entry of the phosphorus into the water body.

Dispersion of large amounts of white phosphorus in air is highly improbable under normal conditions due to its autoignition characteristics. However, problems may result from dispersion of its oxidation products (primarily P_4O_{10}) which will rapidly react with the moisture of the air, forming phosphoric acid as the ultimate product. Red phosphorus, on the other hand, could be dispersed by wind or by an accident-associated deflagration of insufficient energy to cause ignition. Widespread dispersion of relatively small amounts of the red allotrope is not thought to be a significant environmental concern. Localized spills of red phosphorus can easily be recovered by personnel with shovels or other mechanical means.

Factors considered for a white phosphorus spill are depicted below:



5.2 Leak Nomograms

Leak nomograms have not been prepared for white phosphorus because it is doubtful they would ever be of any practical use. Even though the phosphorus contained in a tank car is primarily in liquid form, it is speculated the leak rate can be influenced by the application of cold water directly to the leakage point. This would not only extinguish the ignited material but could help to solidify the liquid and ultimately seal the opening. This may not be possible with a large puncture, but in this case leakage may be so rapid that attempting to calculate the rate of discharge and percent remaining may be fruitless. Also, attempting to approximate the size of the actual opening to the liquid may be impossible due to the reduced visibility resulting from the dense cloud of combustion products and/or the water being applied to the puncture area and the spilled phosphorus. Applying cold water to the leak area is a recommended procedure for sealing a puncture

in a tank car; water is also recommended to extinguish the burning phosphorus and break down the cloud of combustion products.

It is anticipated that the amount of phosphorus remaining in the tank car can be estimated by visibly inspecting the spill area (land only) and estimating the amount spilled. Simple arithmetic will give a very approximate amount remaining in the damaged tank car. Using proper precautions to prevent reignition at the leak site, the hole can be sealed with a temporary patch. The shipper will have been notified and will recommend the procedures involved and possibly carry out the recovery operation for the phosphorus remaining in the tank car. If liquid phosphorus was spilled into water, the amount spilled would not be readily discoverable by visual inspection. The same procedure to cause self-sealing will probably have been carried out; if so, it can be assumed the level of liquid in the tank car is somewhere between its original level (known) and the top of the puncture. Other factors such as duration of flow and an approximate rate can surely narrow down the position of the liquid level. Regardless of the exact level, the tank car still contains white phosphorus and must be treated accordingly.

5.3 Dispersion in the Air

The ability of elemental phosphorus to exist in air has already been established. That its concentration in a confined space may reach a level of concern with respect to toxicity is possible, but widespread dispersion at significant concentrations is not too probable. However, all proper precautions should be initiated as standard operating procedure; measuring stations should be established according to standard guidelines. The primary concerns under normal conditions will be containment of spilled material, extinguishment of ignited material, leak stoppage, monitoring of combustion cloud movement, and cleanup.

Although phosphorus, white or red, is a relatively nonvolatile material, a spill of the liquid or solid white allotrope poses a significant hazard since it spontaneously ignites on contact with air to form a cloud of combustion products. Ignition of red phosphorus will form the same combustion products. Therefore, only the combustion products are treated in this section.

The primary product from the combustion of white (or red) phosphorus is phosphorus pentoxide (P_4O_{10}); phosphorus trioxide (P_4O_6) and possibly other lower oxides may be present under conditions of a limited supply of air (oxygen). Some of the lower oxides have been characterized to some extent, whereas phosphorus trioxide has been comparatively well characterized with respect to structure, chemical reactions and

decomposition products. Phosphorus pentoxide will be dealt with in this section because it is thought to be the major, and possibly the only, combustion product.

Due to the nature of the pentoxide, the vapour dispersion models described in the Introduction Manual cannot be employed directly to determine the downwind and crosswind hazard distances. The phosphorus pentoxide formed during the combustion of phosphorus is a fume (particulate white cloud) and not a vapour. The particle size distribution of fumes arising from burning phosphorus is not known. This is compounded by the fact that the oxides present, primarily phosphorus pentoxide, are very powerful dessicants and react with moisture in air to form phosphoric acid or precursors thereto. This therefore increases the mass of the cloud and helps to maintain its opaqueness (Steubing 1980). Furthermore, the initial cloud will tend to move vertically due to the intense heat generated by the burning white phosphorus.

Some of the known properties of phosphorus trioxide should also be mentioned so that response personnel are familiarized with all possibilities. The material melts at 23.8°C and boils at 175°C. It reacts violently with air (oxygen), a situation that may be encountered when phosphorus is initially combusted in a limited air supply and the heated product cloud then exposed to an unlimited air supply. The product of this oxidation most certainly is the pentoxide. The trioxide decomposes above 210°C to red phosphorus and P_4O_8. This process would certainly produce P_4O_{10} in the presence of oxygen. In cold water, the trioxide slowly forms phosphorous acid (H_3PO_3) which is not thermally stable. This decomposition produces phosphoric acid (H_3PO_4) and phosphine (PH_3). The reaction of the trioxide with hot water is violent and produces red phosphorus, phosphine and phosphoric acid. In addition to its reactiveness, the trioxide is very poisonous (Cotton 1972; Merck 1983; Sax 1979).

Accurately modelling the dispersion of a cloud of phosphorus combustion products is difficult, since no specific data concerning the physical and chemical parameters were found in the normally accessible literature. In the absence of these data, assumptions will have to be made about the following parameters:

- spread rate (spill size)
- emission rate of combustion products
- thermal buoyancy of emitted particulate plume
- rate of formation of phosphoric acid or its precursors in the emitted fume
- agglomeration/sedimentation rate of particulate components of plume

In most cases, these assumptions would only be gross estimates and would have virtually no relationship to a real spill situation. This being the case, no example or sample calculations are presented.

5.4 Behaviour in Water

When liquid phosphorus is spilled into water, it will sink and solidify; some of the material will dissolve. During this process, the liquid mass may partially break up, forming small pieces and possibly some colloidal white phosphorus. Phossy water, which contains both dissolved and colloidal white phosphorus, will be discussed in more detail in Section 6.1.1. Because of the very low solubility of white phosphorus in water, no nomograms have been prepared to describe its behaviour in water.

5.5 Subsurface Behaviour: Penetration into Soil

Neither white phosphorus (solid or liquid) nor red phosphorus (solid) are considered to represent a significant source of groundwater contamination when spilled onto soil. The former liquid will solidify, initially at the soil-liquid phosphorus interface, before any significant movement into the soil will occur. Concurrently, the phosphorus-air interface will under most circumstances be undergoing oxidation, with the emission of a voluminous cloud of predominantly phosphorus pentoxide. A similar combustion process will also occur with any spilled/dumped solid white allotrope. Spilled red phosphorus will remain a solid powder unless ignited. Red phosphorus is insoluble in water; therefore, no movement due to soluble species is considered. The white allotrope, on the other hand, is soluble to a very small extent, but even this is not considered to be a significant problem if proper precautions are taken. It should be noted, however, that liquid phosphorus will migrate to some extent if the nature of the ground material is appropriate. For example, gravel, railroad ballast, or any material of a very porous nature are particularly vulnerable. It is expected that the spill area, along with any unreacted white phosphorus and contaminated water, will be cleaned up within a relatively short period of time. Therefore, significant dissolution and downward movement are not probable under spill conditions involving only phosphorus (either allotrope) and water (added for firefighting purposes or from precipitation). Other accident conditions are possible that may change the above scenario completely, but speculation with regard to these possibilities is not considered in this manual. No soil penetration nomograms are presented.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water Environment - General. As shown earlier, white phosphorus has a low solubility in water; red phosphorus is insoluble. The behaviour of the former in aqueous solution, however, is important, since severe impact occurs in aquatic systems at concentrations well below its solubility limit. No specific data concerning the red allotrope were found. White phosphorus enters the aquatic environment as phossy water which is generated wherever white phosphorus is manufactured, stored under water, or spilled, whether into water or onto land, and where the resulting fire is extinguished with water and the residual phosphorus is covered with water. Phossy water contains dissolved and colloidal white phosphorus as well as larger suspended particles. Data from manufacturing and munitions loading plants indicate that much of the white phosphorus in phossy water is dispersed or colloidal rather than dissolved. The mixture, whether dissolved, dispersed or colloidal, reacts with dissolved oxygen and hydroxide ion to form various oxides, acids and phosphine. In high concentration as a suspension, it results in low to zero dissolved oxygen in the surrounding water; unreacted particles settle out and can be incorporated into aquatic sediments. These particles, when buried in anoxic sediments, are stable for long periods of time.

Data on reaction kinetics and decomposition products of white phosphorus in water are poorly defined. Rates for the oxidation in water vary greatly and seem to depend on pH, dissolved oxygen content, temperature, metal ions, and on the degree of dispersion of colloidal or suspended material if the solubility is exceeded. Estimates of the half-life of white phosphorus in aerated water range from 0.85 h at 30°C for a 1 ppm initial concentration in distilled water, to 10 d or greater for suspensions at higher concentrations or in the presence of iron. Specifically, the half-lives in seawater and freshwater for an initial concentration of 1-50 ppm at 0°C were determined to be 240 and 150 h, respectively. A major factor controlling the rate of disappearance of white phosphorus apparently is whether it is suspended or dissolved. At concentrations below the solubility limit, and where a majority of the material is dissolved, it initially oxidizes in aerated water via a first order reaction to concentrations below 0.01 ppm. The material continues to slowly oxidize to equilibrium levels of 0.04 to 0.10 ppb. Other preliminary results, however, suggest that white phosphorus at low concentrations rapidly oxidizes to below 0.01 ppb. The disappearance rate from more concentrated suspensions

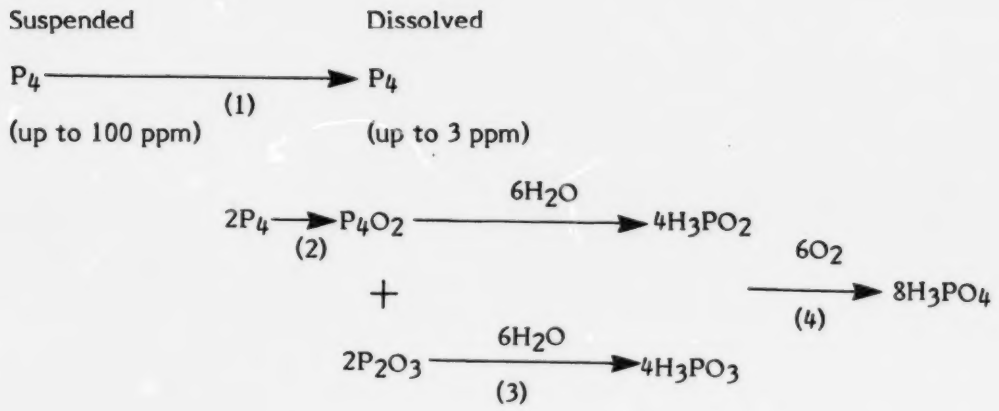
apparently is controlled by diffusion and the protection of the phosphorus from the dissolved oxygen. It has been shown that saline water may influence the reaction rate. The authors suggested that perhaps salts coagulate the colloidal particles and make them less accessible to oxygen.

It is apparent that many factors influence the oxidation rate of white phosphorus in water. Since it is not the purpose of this manual to present in detail the various data on the subject, the reader is referred to the primary reference used for a brief explanation of phossy water (Sullivan 1979).

A further brief explanation of the oxidation products from white phosphorus in an aqueous environment in thought worthwhile at this time. It is suggested that white phosphorus in aqueous solution may oxidize in a single step or react stepwise to form several oxides that are ultimately converted to phosphate as phosphoric acid. Possible intermediate compounds formed during the conversion of P_4 to PO_4^{-3} are:

Hypophosphite ($H_2PO_2^-$)
Hydrophosphite (HPO_3H^{-1})
Phosphite (HPO_3^{-2})
Pyrophosphate ($P_2O_7^{-4}$) (linear)
Tripolyphosphate ($P_3O_{10}^{-5}$) (linear)
Trimetaphosphate ($P_3O_9^{-3}$) (cyclic)
Tetrametaphosphate ($P_4O_{12}^{-4}$) (cyclic)
Hexametaphosphate ($P_6O_{18}^{-6}$) (cyclic)
Phosphine (PH_3)

A recent work suggests the oxidation of white phosphorus in water follows a stepwise path and that P_4O_{10} is not a primary product. The main products identified were hypophosphorous acid (H_3PO_2), phosphorous acid (H_3PO_3) and orthophosphoric acid (H_3PO_4). Apparently, a rapid reaction occurs to form the lower oxidation state oxides which hydrolyze to form the oxyacids; however, complete oxidation to orthophosphoric acid is slow. In addition, elemental phosphorus can react to form phosphine (PH_3), especially at high pH. The latter is presumed to be lost to the atmosphere or to quickly react to a higher oxidation state, resulting in an extremely small amount in phossy water. The chemical behaviour of white phosphorus in water can be diagrammed as follows:



where (1) = Diffusion-controlled pathway. Rate is dependent on particle size, agitation and other factors.

(2) = First order kinetics; k (base e) ≈ 0.1-0.7/h for disappearance of P_4 in distilled water.

(3) = Very rapid hydrolysis to oxyacids.

(4) = Slow oxidation to phosphate (Sullivan 1979).

6.1.2 Water Environment - Limits. Bioassay and field data suggest acute and chronic effects on aquatic biota are significant at concentrations well below 10 µg/L. Federal (U.S.) regulations limit the discharge of white phosphorus to the Arkansas River to 10 µg/L (from Pine Bluff Arsenal) (Sullivan 1979). The recommended drinking water limit is 0.1 ppm (OHM-TADS 1981).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. The aquatic toxicity rating, TL_m96, of white phosphorus is less than 1 mg/L (RTECS 1979). No value was given for red phosphorus.

The following general summary of measured toxicity data was extracted from Sullivan (1979). Since not all data were extracted, the reader is advised to refer to the above work and, in turn, to the original work for a more detailed review. Little or no data were found for red phosphorus.

Considerable work has been accomplished with respect to the toxic effects of white phosphorus on aquatic life. Fish appear to be the most sensitive group of freshwater aquatic organisms. Static and flow-through acute bioassays of white phosphorus using bluegill and channel catfish as test organisms were conducted. Static acute tests were also conducted using rainbow trout, fathead minnow and mosquito fish.

Chronic studies were also carried out in embryo-larvae (egg-fry) tests using catfish and fathead minnow as test species. All static and flow-through acute bioassays reported by Bentley (1978) were based on nominal white phosphorus concentrations, as was the fathead minnow egg-fry study. Concentrations of white phosphorus in chronic bioassays for the fathead minnow represented measured concentrations; this was also the case with the Pearson (1978) bioassay results. The bluegill, used to test the effects of changes in temperature, pH and water hardness, was the organism most sensitive to the acute effects of white phosphorus. Low pH or high hardness decreased the sensitivity of the bluegill to the material. The duration of exposure greatly influenced the LC_{50} for the two fish tested under flow-through conditions. Incipient LC_{50}s for the bluegill and channel catfish were 5 and 17 times lower, respectively, than the 96-h static LC_{50}s.

Eggs were the most resistant life stage under static conditions. Susceptibility of this organism increased with age. The 60-day-old fry were the most sensitive age group, with the 96-h LC_{50} being similar to that of adult fish. A more detailed summary of these data can be gained from Sullivan (1979).

White phosphorus is acutely toxic to euryhaline fish at concentrations in the same range as for freshwater forms. No-effect levels for the two species tested were below the lowest concentrations tested. The investigators concluded that toxic effects to these species were dose-related (a function of time and concentration) rather than related strictly to concentration (Sullivan 1979). Several marine species were tested; cod was found to be approximately as sensitive as bluegill, the most sensitive freshwater species. No-effect levels were not defined for marine fish since the lowest concentrations tested (1.89 µg/L) caused mortalities (Sullivan 1979).

Fish species consuming white phosphorus in the form of prey fish exhibited symptoms of phosphorus poisoning without actually coming into direct contact with contaminated water (NRCC 1981).

The toxicity of white phosphorus to four species of freshwater algae was investigated. Chlorophyll *a* concentrations and either cell numbers or optical density relative to control cultures were used as measures of growth response in cultures exposed to nominal concentrations of white phosphorus ranging from 7 to 670 µg/L. The pattern of growth response for each species is summarized in Section 6.2.2.1. The algae tested did not apparently exhibit a consistent growth-response to white phosphorus; an acute toxic level (EC_{50} and LC_{50}) was therefore not reported. The data suggest the mode of effect of the material on procaryotic cells differs from the effect on more highly organized eucaryotic cells. The acute response levels suggest that freshwater algae are

less sensitive to white phosphorus than are fish. The no-effect level for *Navicula* was between nominal concentrations of 7 and 20 µg/L (Sullivan 1979).

Bioconcentration factors of 22X and 23X for two marine species, *Fucus distichus* and *Fucus vesiculosus*, exposed to measured white phosphorus concentrations of 15 + 9.0 µg/L for 48 hours under flow-through conditions were reported (Fletcher 1971. IN Sullivan 1979). Seven days after transfer to white-phosphorus-free seawater, no detectable levels of elemental phosphorus (<0.002 µg/g) were found in the tissues of either species. No toxic effects to the algae during or after exposure were reported (Sullivan 1979).

Acute toxicity studies demonstrated that white phosphorus is toxic to freshwater invertebrates. Acute toxicity tests of 48 hours duration under static conditions were conducted on three species of macroinvertebrates and one zooplankton species. In other testing, preliminary 48- and 96-h static bioassays of white phosphorus were conducted using four other macroinvertebrates. These total organisms are representative of the broad spectrum of invertebrate forms found in freshwater ecosystems. Also, flow-through tests were conducted in order to define incipient EC_{50} values for *Daphnia* and for *Chironomus* larvae. These data are summarized in Section 6.2.2.1. The general findings seem to indicate that invertebrates are less sensitive than fish to the acute effects of white phosphorus. Chronic studies (Bentley 1978. IN Sullivan 1979) over two generations of *Daphnia magna* indicated that up to 6.9 µg/L of white phosphorus produced no effects. The maximum allowable toxicant concentration (MATC*) for this organism was found to lie between 6.9 and 8.7 µg/L elemental phosphorus (Sullivan 1979).

Limited bioassay results for two marine invertebrates are shown in Section 6.2.2.3. Incipient lethal levels for the marine *Gammarus* species were about 1000 times the level for a freshwater form of the same genus. It was shown that the amphipod can recover from short-term exposure to fairly high concentrations of white phosphorus:

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*MATC: The highest concentration of toxicant that has no adverse effect on survival, growth or reproduction of a species, based on the results of a life-cycle toxicity test. A life-cycle or partial life-cycle test cannot produce a value for the MATC; a test can only produce limits within which the MATC must fall.

Conc. (µg/L)	Exposure Time (h)	% Recovery
8	3	100
17	1	90
40	1	20

Toxicity to lobsters, however, is apparently irreversible. The incipient LC_{50} was estimated to be between 20 and 40 µg/L. The latter value range was the result of an investigation of the toxicity of white phosphorus released from actual contaminated sediment. The investigators reported that the response in lobsters was a function of the product of exposure time and concentration. It was also shown that sublethal exposure of the lobster to the chemical did not affect molting. In general, marine invertebrates do not appear to be as sensitive to white phosphorus toxicity as both freshwater and marine fish (Sullivan 1979).

6.2.2 **Measured Toxicities** (Static and Flow-through).

6.2.2.1 **Freshwater toxicity** (Acute).

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
Fish Toxicity Tests - Static					
0.061	24	Rainbow trout	LC_{50}		Bentley 1978
0.028	48	Rainbow trout	LC_{50}		Bentley 1978
0.022	96	Rainbow trout	LC_{50}		Bentley 1978
0.063	96	Mosquito fish	LC_{50}		Pearson 1978
0.152	24	Channel catfish	LC_{50}		Bentley 1978
0.087	48	Channel catfish	LC_{50}		Bentley 1978
0.101	24	Fathead minnow	LC_{50}		Bentley 1978
0.036	48	Fathead minnow	LC_{50}		Bentley 1978
0.020	96	Fathead minnow	LC_{50}		Bentley 1978
>0.560	24	Fathead minnow, eggs	LC_{50}		Bentley 1978

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
>0.560	48	Fathead minnow, eggs	LC_{50}		Bentley 1978
>0.560	96	Fathead minnow, eggs	LC_{50}		Bentley 1978
0.154	96	Fathead minnow, fry, 1 h post-hatch	LC_{50}		Bentley 1978
0.074	96	Fathead minnow, fry, 7 d post-hatch	LC_{50}		Bentley 1978
0.021	96	Fathead minnow, fry, 30 d post-hatch	LC_{50}		Bentley 1978
0.018	96	Fathead minnow, fry, 60 d post-hatch	LC_{50}		Bentley 1978
0.027	24	Bluegill	LC_{50}		Bentley 1978
0.009	48	Bluegill	LC_{50}		Bentley 1978
0.029	96	Bluegill	LC_{50}	Dechlorinated tap water, TH*= 50-60	Pearson 1978
0.072	96	Bluegill	LC_{50}	Dechlorinated tap water, TH= 50-60	Isom 1960
0.006	96	Bluegill	LC_{50}	Dechlorinated tap water, TH = 50-60	Bentley 1978
0.025	163	Bluegill	LC_{50}	Dechlorinated tap water, TH = 50-60	Bentley 1978
0.005	96	Bluegill	LC_{50}	T = 15°C, pH = 7.0, TH = 35	Bentley 1978

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
0.005	96	Bluegill	LC_{50}	T = 20°C, pH = 7.0, TH = 35	Bentley 1978
0.002	96	Bluegill	LC_{50}	T = 25°C, pH = 7.0, TH = 35	Bentley 1978
0.005	96	Bluegill	LC_{50}	T = 20°C, pH = 7.0, TH = 35	Bentley 1978
0.004	96	Bluegill	LC_{50}	T = 20°C, pH = 7.0, TH = 100	Bentley 1978
0.086	96	Bluegill	LC_{50}	T = 20°C, pH = 7.0, TH = 250	Bentley 1978
0.069	96	Bluegill	LC_{50}	T = 20°C, pH = 6.0, TH = 35	Bentley 1978
0.008	96	Bluegill	LC_{50}	T = 20°C, pH = 7.0, TH = 35	Bentley 1978
0.004	96	Bluegill	LC_{50}	T = 20°C, pH = 8.0, TH = 35	Bentley 1978
Fish Toxicity Tests - Flow-through					
>0.0032	24	Bluegill	LC_{50}		Bentley 1978
0.0024	96	Bluegill	LC_{50}		Bentley 1978
0.006	192	Bluegill	LC_{50}	Incipient LC_{50}	Bentley 1978
>0.019	24	Channel catfish	LC_{50}		Bentley 1978
>0.019	96	Channel catfish	LC_{50}		Bentley 1978
0.0042	624	Channel catfish	LC_{50}	Incipient LC_{50}	Bentley 1978

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
Invertebrate Toxicity Tests - Static					
0.034	24	Cladoceran (*Daphnia magna*)	EC_{50}		Bentley 1978
0.030	48	Cladoceran (*Daphnia magna*)	EC_{50}		Bentley 1978
0.038	48	Oligochaete	EC_{50}	Preliminary bioassay	Pearson 1978
0.0596	48	Glass shrimp (Mysid)	EC_{50}		Pearson 1978
0.032	96	Glass shrimp (Mysid)	EC_{50}		Pearson 1978
>0.420 <0.560	24	Amphipod	EC_{50}		Bentley 1978
0.250	48	Amphipod	EC_{50}		Bentley 1978
>0.560	24	Isopod	EC_{50}		Bentley 1978
>0.560	48	Isopod	EC_{50}		Bentley 1978
0.038	48	Phantom midge	EC_{50}	Preliminary bioassay	Pearson 1978
0.260	24	Midge (*Chironomus tentans*)	EC_{50}		Bentley 1978
0.140	48	Midge (*Chironomus tentans*)	EC_{50}		Bentley 1978
0.308	48	Midge (*Glyptotendipes* sp.)	EC_{50}	Preliminary bioassay	Pearson 1978
Invertebrate Toxicity Tests - Flow-through					
>0.050	24	Cladoceran (*Daphnia magna*)	EC_{50}		Bentley 1978
>0.050	48	Cladoceran (*Daphnia magna*)	EC_{50}		Bentley 1978
0.011	192	Cladoceran (*Daphnia magna*)	EC_{50}	Incipient EC_{50}	Bentley 1978
>0.240	24	Midge (*Chironomus tentans*)	EC_{50}		Bentley 1978
0.111	48	Midge (*Chironomus tentans*)	EC_{50}		Bentley 1978

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference
0.020	120	Midge (*Chironomus tentans*)	EC_{50}		Bentley 1978. IN Sullivan 1979

* TH = Total Hardness, mg/L $CaCO_3$.

Plant Toxicity (Bentley 1978. IN Sullivan 1979)

	Response** to Increasing P_4 Concentrations at		
Algal Species Tested	24 h	48 h	96 hrs: EC_{50}
Eucaryotes:			
Navicula pelliculosa	inhibition	inhibition	inhibition: 60-80 µg/L
Selanostrum capricornutum	stimulation	inhibition	inhibition: >200 µg/L
Procaryotes:			
Microcystis aeruginosa	stimulation	stimulation	stimulation: >100 µg/L
Anabaena flos-aquae	stimulation	stimulation	stimulation: >100 µg/L

** Measured as either cell numbers or optical density, or chlorophyll a concentration relative to controls receiving no P_4.

6.2.2.2 Euryhaline toxicity (Acute).

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
Fish Toxicity Tests - Static					
0.018	Not reported	Atlantic salmon	LC_{50}	Seawater bioassay, incipient LC_{50}	Zitko 1970

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
Fish Toxicity Tests - Flow-through					
~0.0026	96	Brook trout	LC_{50}	Seawater bioassay	Fletcher 1970
0.00050	200	Brook trout	LT_{50}	Seawater bioassay	Fletcher 1970
~0.0023	96	Atlantic salmon	LC_{50}	Seawater bioassay	Fletcher and Hoyle 1972
0.00079	195	Atlantic salmon	LT_{50}	Seawater bioassay	Fletcher and Hoyle 1972
0.0228	50.2	Atlantic salmon	LT_{50}	Freshwater bioassay	Fletcher and Hoyle 1972

6.2.2.3 Marine toxicity (Acute).

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
Fish Toxicity Tests - Static					
~0.0037	96	Atlantic herring	LC_{50}		Zitko 1970
Fish Toxicity Tests - Flow-through					
0.0144	48	Atlantic cod	LC_{50}	Dissolved P_4	Maddock and Taylor 1976
~0.0025	96	Atlantic cod	LC_{50}		Fletcher and Hoyle 1972
0.00189	125	Atlantic cod	LT_{50}		Fletcher and Hoyle 1972
0.100	3.6	Atlantic herring	LT_{50}		Fletcher 1972
0.0900	85.2	Mummichog	LT_{50}	Preliminary bioassay	Fletcher 1971

Conc. (mg/L) (White P_4)	Time (hours)	Species	Result	Water Conditions	Reference (All IN Sullivan 1979)
0.0202	102	Mummichog	LT_{50}	Preliminary bioassay	Fletcher 1971
0.1000	14	Cunner	LT_{50}	Preliminary bioassay	Fletcher 1971
0.0228	19	Cunner	LT_{50}	Preliminary bioassay	Fletcher 1971
0.0740	23	Cunner	LT_{50}	Preliminary bioassay	Fletcher 1971
0.0005	171	Cunner	LT_{50}	Preliminary bioassay	Fletcher 1971
0.0034	190	Cunner	LT_{50}	Preliminary bioassay	Fletcher 1971
Invertebrate Toxicity Tests - Static					
>3.000 <4.000	24	Amphipod	EC_{50}	Preliminary bioassay, incipient EC_{50}	Zitko 1970
>0.020 <0.040	168	American lobster	EC_{50}	Incipient EC_{50}, P_4 released from contaminated sediments	Zitko 1970
Invertebrate Toxicity Tests - Flow-through					
0.0230 ± 0.0060	620	American lobster	LT_{50}		Fletcher 1971
~6.500	24	Amphipod	EC_{50}	Incipient EC_{50}	Zitko 1970

6.2.3 Measured Toxicities (Bioaccumulation). This general summary concerning the bioaccumulation of white phosphorus was primarily extracted from Sullivan (1979). The reader is thus directed to this work for a more detailed analysis. Other references will be quoted as used.

The accumulation of white phosphorus in the tissues of aquatic organisms has been documented by many investigators, especially with regard to marine life. Acute lethal doses are strongly time-dependent. The delayed but inevitable death of organisms exposed for short periods to high concentrations or for long periods to very low concentrations suggests a possible bioaccumulatory mechanism (Sullivan 1979).

It has been shown that the liver of fish (especially liver oil in cod) is the organ which accumulates the largest amount of phosphorus. Concentration factors in this organ ranged from less than 12 to 58 000. This latter value, however, may have been an artifact of the manner in which the fish (cod) were exposed rather than a true concentration factor. The cod did have by far the highest liver bioconcentration factor. It was speculated this was due to the exceptionally high content of lipids in the liver of this species; bioconcentration in the organs of fish apparently relates to their relative lipid content (Sullivan 1979).

It has been shown that white phosphorus in fish tissue disappears rapidly from living fish after removal from contaminated water. The half-life of white phosphorus in salmon (*Salmo salar*) exposed to 1.6 mg/L for 40 min was estimated to be 0.90-1.02 h for the liver and 2.71-5.54 h for intestinal contents. In the cod (*Gadus morrhua*), the half-life was estimated to be 4-13 h in the liver and 4.7 and 6.2 h in muscle and blood, respectively. Exposure conditions for the cod were similar to those for the salmon. Relatively constant concentrations of white phosphorus appeared to be reached in cod tissues after 12-24 h exposure to 8 µg/L (Sullivan 1979).

Marine macroinvertebrates survived exposure to white phosphorus but concentrated the material up to 42 times the water concentration (15 µg/L). The data seemed to indicate the bioconcentration factor is related directly to relative lipid content since the periwinkle has the highest overall lipid content of the mollusks. The distribution of tissue concentrations of white phosphorus was also directly dependent on tissue lipid content in the starfish and the lobster. Also, the organisms quickly lost their accumulated white phosphorus content after transfer to uncontaminated water. The general depuration period for shellfish and lobster was 7 days (Sullivan 1979).

In general, white phosphorus becomes concentrated to levels 20 to 100 times above ambient in the tissues of aquatic organisms (several thousand times in liver tissue of cod). This effect does not represent a bioaccumulation in the sense that pesticide residues permanently lodge in tissue. White phosphorus remains mobile; consequently, its concentration rapidly decreases after transfer of a contaminated organism to clean water (Sullivan 1979).

6.2.3.1 Freshwater bioconcentration.

Exposure Conc. (mg/L) (White P_4)	Time (days)	Species	Tissue Bioconcentration Factor			Remarks	Reference (All IN Sullivan 1979)
			Muscle	Liver	Other Viscera		
Fish Bioconcentration Tests							
0.046	0.67 (16 h)	Bluegill	-	44	-	Analysis of pooled tissue from 16 fish	Pearson 1976
Not reported	Not reported	Freshwater drum	-	69	-	Environmental field samples, Pine Bluff Arsenal	Pearson 1976
0.0022 ± 0.00031	1-7	Fathead minnow	<45-155	-	<82-200 (Includes liver tissue also for this species)	-	Bentley 1978
Not reported	Not reported	Channel catfish	-	44	-	Environmental field samples, Pine Bluff Arsenal	Pearson 1976

Exposure Conc. (mg/L) (White P_4)	Time (days)	Species	Tissue Bioconcentration Factor			Remarks	Reference (All IN Sullivan 1979)
			Muscle	Liver	Other Viscera		
0.0018 ± 0.00023	1-47	Channel catfish	(239) 50-106	<12-67	44-106	The single value of 239 resulted from replicates of 78 and 394	Bentley 1978
0.00018 ± 0.00002	1-47	Channel catfish	31-94	not detected	<27-100	Tissue concentrations were generally barely detectable	Bentley 1978

Invertebrate Bioconcentration Tests

None reported.

Plant Bioconcentration Tests

See Section 6.2.2.1

6.2.3.2 Euryhaline bioconcentration.

Exposure Conc. (mg/L) (White P_4)	Time (days)	Species	Tissue Bioconcentration Factor: Muscle	Liver	Other Viscera	Remarks	Reference (All IN Sullivan 1979)
Fish Bioconcentration Tests							
0.0228 to 0.763	Until death* (LT_{50} = 0.1 to 2.1 d)	Atlantic salmon (*Salmo salar*)	24-48	26-91	257-658 (Pyloric caeca)	Fresh-water-maintained (15 fish)	Fletcher 1974
1.900	Until death (LT_{50} = 0.1 d)	Atlantic salmon (*Salmo salar*)	12	27	29 (Pyloric caeca) 56 (Brain) 16** (Blood)	Sea-water-maintained (95 fish)	Fletcher 1974
0.00079 to 1.900	Until death (LT_{50} = 0.1 to 8.1 d)	Atlantic salmon (*Salmo salar*)	20	41	28***	Sea-water-maintained (95 fish)	Fletcher 1974
Invertebrate Bioconcentration Tests							
None reported.							
Plant Bioconcentration Tests							
None reported.							

* No individual data given. Median lethal time (LT_{50}) reported.
** Blood analysis: Bioconcentration factor; 40X in erythrocytes, 5X in plasma.
*** Average bioconcentration factor for pyloric caeca, esophagus, intestine, gill and kidney tissues.

6.2.3.3 Marine bioconcentration.

Exposure Conc. (mg/L) (White P_4)	Time (days)	Species	Tissue Bioconcentration Factor			Remarks	Reference (All IN Sullivan 1979)
			Muscle	Liver	Other Viscera		
Fish Bioconcentration Tests							
0.001	0.67 (16 h)	Atlantic cod (*Gadus morrhua*)	172 (red)	58 000 (oil)	-	P_4 feedstock too dilute;	Dyer 1970
			71	20 000 (whole liver)	-	P_4 conc. in control tanks without fish reached 20-30 µg/L	
0.021 to 0.083	0.67 (16 h)	Atlantic cod (*Gadus morrhua*)	54-83 (red)	2750-7350 (oil)	-	P_4 feedstock conc. increased to allow P_4 build-up in exposure tanks	Dyer 1970
			9-26	883-2000 (whole liver)	-		
0.630	0.5 h	Atlantic cod (*Gadus morrhua*)	1	68 (oil)	-	-	Dyer 1970
			-	30 (whole liver)	-		
0.00189 to 5.780	Until death* (LT_{50} = 0.06-5.2)	Atlantic cod (*Gadus morrhua*)	44	2460	67**	Calculated from regression equation of tissue P_4 conc. On water conc. r^2 = 0.794 to 0.956	Fletcher 1974
					103 (whole fish)		

Exposure Conc. (mg/L) (White P_4)	Time (days)	Species	Tissue Bioconcentration Factor: Muscle	Liver	Other Viscera	Remarks	Reference (All IN Sullivan 1979)
						for the various organs tested	
0.0044 to 0.029 (10.8)***	Until death (LT_{50} = 0.7-7.3)	Atlantic cod (*Gadus morrhua*)	10-34†	115-281† (2314)***	-	Dissolved P_4 with no colloidal material present	Maddock and Taylor 1976

* No individual data given. Median lethal time (LT_{50}) reported.

** Average bioconcentration factor for pyloric caeca, spleen, testes, ovary, esophagus, intestine and gill tissues.

*** One concentration, 10.8 µg/L, resulted in a liver bioconcentration factor calculated as 2314. All other liver tissues bioconcentration factors ranged from 115 to 281 in the reported studies.

† Calculated from tissue concentration data.

Exposure Conc. (mg/L) (Mean ± Standard Deviation) (White P_4)	Time (days)	Species (No. tested)	Tissue	Tissue Bioconcentration Factor
Invertebrate Bioconcentration Tests (Fletcher 1971. IN Sullivan 1979)				
0.015±0.009	2	Blue mussel (10) (*Mytilus edulis*)	Whole organism (no shells)	10
0.015±0.009	2	Clam (5) (*Mya arenaria*)	Whole organism (no shells)	23
0.015±0.009	2	Periwinkle (10) (*Littorina littorea*)	Whole organism (no shells)	42
0.015±0.009	2	Quahog (5) (*Arctica islandica*)	Whole organism (no shells)	17

Exposure Conc. (mg/L) (Mean ± Standard Deviation) (White P_4)	Time (days)	Species (No. tested)	Tissue	Tissue Bioconcentration Factor
0.015±0.009	2	Starfish (1) (*Asterias vulgaris*)	Whole organism	27
			Pyloric caeca	131
			Body wall	12
			Periovisceral fluid	<1
0.015+0.009	2	American lobster (5) (*Homarus americanus*)	Hepatopancreas	1270
			Ovary	267
			Tail muscle	34
			Chela muscle	26
			Gill	18
			Hemolymph	5
0.023+0.007	Until death (~25 d)	American lobster (5) (*Homarus americanus*)	Hepatopancreas	1970
			Ovary	412
			Tail muscle	31
			Chela muscle	23
			Gill	9
			Hemolymph	4
Plant Bioconcentration Tests				
None reported.				

6.2.4 Toxicity Conclusions. White phosphorus is one of the most highly toxic inorganic substances known. A 1978 study attributed the toxic effect of the material biochemically to its potent reducing power (Sullivan 1979).

The greater susceptibility of eucaryotic cells, as opposed to procaryotic cells, is probably the result of two factors: 1) white phosphorus is lipid-soluble, and 2) the proper functioning of an eucaryotic cell (whether a microorganism, e.g., diatom, or a cell in the liver of a vertebrate) is highly dependent on the spatial organization and compartmentalization of biochemical reactions by the phospholipid membranes of the endoplasmic reticulum. In the former factor, the white phosphorus would be expected to localize in cytoplasmic membrane systems or in lipid storage organelles. If concentrated in the endoplasmic reticulum, it would directly affect membrane-bound enzymatic reactions. Since procaryotic cells contain a much simpler intracellular organization and no internal membranes, they may be expected to be less sensitive to the disruptive effects of the

substance (Sullivan 1979). Other works have similarly stated that acute poisoning by white phosphorus is similar to the effects of other hepatotoxins because it interferes with protein synthesis on the granular endoplasmic reticulum. Additional data, based on studies of the effects of white phosphorus on cultured cells, similarly suggest that the substance strongly affects intracellular organization and membrane-bound protein synthesis, but only slightly affects respiration (Sullivan 1979).

In higher aquatic organisms, white phosphorus enters via the gills (or the intestinal tract), circulates in the blood, and damages all tissues which it contacts. The relative tissue concentrations found in histological studies probably do not relate to white phosphorus effects as much as protection of the substance from reaction by means of adsorption in stored lipid. Damage to the organism appears generally to be related to exposure time x concentration. The rapid cleaning of the material from the organism after it is removed from exposure probably relates to rapid oxidation of the white phosphorus in the body of the organism. This results in further tissue damage even after the organism is removed from the contaminated area (Sullivan 1979).

The gross effects of acute and chronic white phosphorus toxicity to fish generally relate to hemolysis (green intestines, jaundiced livers, and/or reddening of the skin). The primary effect, however, may be due to other factors. The specific symptoms of white phosphorus toxicity vary among fish species (Sullivan 1979).

6.3 Toxicity to Animal Life

In acute poisoning of mammals by white phosphorus, rapid death is due to the effects of shock and from damage to the cardiovascular system. Death occurring within a few days but due to lower doses usually can be attributed to renal or liver failure and from damage to the digestive tract. It has been reported to cause significant damage to the liver, kidneys, central nervous system and the long bones. Damage to the liver is manifested by a dramatic increase in liver fat and a depletion of liver glycogen. Kidney damage was reflected by changes in creatinine clearance, urine flow, and plasma electrolytes. The ganglion cells in the central nervous system show a variety of pathologic changes, including granular disintegration of the Nissl bodies, hyperchromatoxis, and nuclear shrinkage. Nerve cells of the superior olives appear to be the most susceptible to the effects of white phosphorus. It appears to act primarily as a cellular poison as there is no evidence of myelin sheath damage. The long bones are affected by white phosphorus in that the number of trabeculae in the metaphysis are increased, resulting in a zone of increased density visible with X-rays. It appears the threshold

dietary level for inducing retarded growth in rats is in the range 0.003-0.07 mg P_4/kg/d, which is more than 100 times less than the lethal dose (7 mg/kg). Humans appear to be about five times more sensitive than rats to the lethal effects of white phosphorus (NRCC 1981; Sullivan 1979). Red phosphrous is generally considered to be less toxic than the white allotrope. It has, however, been shown to affect the liver and kidneys of test animals in a manner similar to that of white phosphorus (Patty 1981).

6.3.1 Mammalian Toxicity.

Conc. (mg/kg) (White P_4)	Species	Effect	Reference
160	Pig	LD_{LO}; oral	RTECS 1979
2	Dog	LD_{LO}; subcutaneous	RTECS 1979
50	Dog	LD_{LO}; oral	RTECS 1979
10	Rabbit	LD_{LO}; subcutaneous	RTECS 1979
2	Dog	LD_{100}; subcutaneous	OHM-TADS 1981
2-12	Dog	Lethal	NRCC 1981
7	Rabbit	LD_{LO}; oral	OHM-TADS 1981
12.5	Rabbit	LD_{100}; subcutaneous	OHM-TADS 1981
4	Rabbit	Lethal	NRCC 1981
0.5	Rat	LD_{100}; oral	OHM-TADS 1981
7	Rat	Lethal	NRCC 1981
3.5	Mouse	LD_{100}; oral	OHM-TADS 1981
16	Mouse	Lethal	NRCC 1981
200	Mammal	LD_{LO}; oral	RTECS 1979
16	Human	TD_{LO}; oral	RTECS 1979
1.4	Human	LD_{LO}; oral (lethal)	RTECS 1979; NRCC 1981
2.6	Woman	TD_{LO}; oral	RTECS 1979

6.3.2 Avian Toxicity. Minimal data were found with regard to avian toxicity. Ducks have shown both kidney (necrosis) and blood (red cells degenerate; many juvenile cells) effects when 1-12 mg/kg of white phosphorus was placed in the gizzard tube (NRCC 1981).

Conc. (mg/kg) (White P_4)	Time (h)	Species	Result	Reference
3	6 to 33	Duck	Lethal; oral. (Shown as LD_{100} in OHM-TADS 1981)	Ducre 1974

6.4 Environmental Fate and Effects

6.4.1 Freshwater Environment. Conclusions resulting from field studies of the environmental fate and effects of white phosphorus in freshwater ecosystems were derived from work by the U.S. Army Material Development and Readiness Command (Pine Bluff Arsenal, Arkansas) and Monsanto, Inc. (Columbia, Tennessee). White phosphorus in freshwater environments appears to be distributed between the sediments and the water column. Fish responded to changes in white phosphorus concentrations in the water within a matter of hours and concentrated the material some 30-50 times in their livers. Dead fish were observed with liver concentrations ranging from 2000 to 8000 µg/kg. Fish surviving spikes of white phosphorus apparently eliminate the material from their tissues to a level in equilibrium with the prevailing white phosphorus concentration. Spikes in white phosphorus concentrations in the water bodies under study occurred after storms. It was strongly suggested that storm events increased the white phosphorus concentrations by either increasing the input from another nearby source by overflow or by resuspension of sediments rich in white phosphorus, or both mechanisms. In aquatic sediments, the presence of up to 0.6 µg/kg on a wet weight basis did not produce an observable effect on a benthic community dominated by midge larvae. Sediment concentrations above 2 µg/kg (range 2-43.3 µg/kg) on a wet weight basis drastically altered benthic community structure (Sullivan 1979).

6.4.2 Marine Environment. The conclusions reached for the marine environment result from studies carried out by the Fisheries Research Board of Canada at

Plancentia Bay, Newfoundland. The data taken during this study suggest that concentrations of white phosphorus greater than 1 µg/L in water do not persist for appreciable periods of time. Sediment concentrations, however, are stable; resuspension may provide a source to maintain 0.5-1.0 µg/L in overlying water. These concentrations apparently affect fish populations and allow bioaccumulation of up to 10-40 times in the flesh of herring. Sediment concentrations above 70 µg/kg and water concentrations of 3 µg/L are associated with impacts on the invertebrate community in the form of selected mortalities. No concentration or dose-effect relationship was defined for the acute effects of fish kills (1969) or *Littorina littorea* (periwinkle) disappearance in Long Harbour (Sullivan 1979).

6.4.3 Theoretical Oxygen Demand (ThOD). Complete combustion of white phosphorus in air results in the formation of phosphorus pentoxide (P_4O_{10}). The other allotropes should give the same product, if ignited. White phosphorus will also react with dissolved oxygen in water to a point where its concentration is very low. These low concentrations persist for extended periods of time. Estimates of the half-life of white phosphorus in aerated freshwater range from 0.85 h, at 30°C for a 1 ppm initial concentration in distilled water, to 10 days or greater for suspensions at higher concentrations, and 2 h at 10°C for a concentration of 2 µg/L in seawater. Particles buried in anoxic sediments are stable for long periods of time. Discharge of a phosphorus manufacturing plant process water containing up to 1 percent white phosphorus directly into Long Harbour apparently created a layer of low to zero dissolved oxygen in the bottom waters over contaminated sediment (Sullivan 1979; NRCC 1981). The theoretical oxygen demand for white phosphorus is 1.29. The following equation was used:

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

Section 6.1.1 gives a more complete explanation of the oxidation process in the aqueous environment.

Commercial red phosphorus is much more stable than the white allotrope; on exposure to air, however, it reacts slowly and exothermically with oxygen and water vapour. This sometimes gives rise to spontaneous combustion in large storage piles (Kirk-Othmer 1981). No data were found with regard to its long-term fate in water.

6.4.4 Food Chain Concentration. White phosphorus bioaccumulates in live fish which are exposed to water containing the material. Furthermore, the concentrations of white phosphorus in tissues of test fish at death appeared to vary directly with the concentration of the substance in the water. Concentrations of white phosphorus in

tissues of fish decrease rapidly when the fish are removed from the contaminated water. This latter effect probably results from rapid oxidation of the white phosphorus in the organism. The general half-life of white phosphorus in various fish tissues has been established:

Condition	P_4 Conc.	Temp. (°C)	Approximate Half-life
Dead	1-5 mg/kg	frozen	2-3 months
Dead	<700 µg/kg	frozen	stable
Live	1-100 mg/kg	5-10	1-6 hours

It has also been shown that the concentrations of white phosphorus in various tissues could be toxic or lethal if the fish tissues were eaten by mammals (including humans) and other fish (NRCC 1981; Sullivan 1979). This transfer of white phosphorus from one contaminated organism to another cannot be considered food chain contamination in the same sense as encountered with pesticides. Certainly this transfer process will not be long-lived under most conditions due to the reactivity of the element. In the true sense of long-term food chain contamination, the potential from white phosphorus is considered nil. No data were found regarding red phosphorus.

6.4.5 Soil Degradation of Material. Experiments with white phosphorus have shown that it can readily escape from soil as the unoxidized vapour. Soil pH seems to have little effect on the amount that escapes or on the relative abundance of oxides versus element. The amount that escapes seems to be more related to depth of a point source placement than to soil type. Escape of vapour was reduced with depth of point source. More elemental phosphorus vapour than oxides was recovered from the atmosphere. Also, soil moisture content has relatively little effect on the amount of vapour released or the vapour/oxide ratio. It appeared the tendency of the oxides to escape was significantly less than that of the element (Warwick 1972). It seems reasonable to conclude that any significant soil penetration by molten white phosphorus as the result of a spill will result in the emission of white phosphorus vapour from the spill site unless the contaminated soil is removed or the phosphorus is oxidized on site. Some oxidation in the soil will occur naturally, but the experiments showed that significant amounts of the original phosphorus that was placed in the soil was released from the soil as vapour and this occurred for several days.

7 HUMAN HEALTH

There is a substantial amount of information in the published literature concerning the toxicological effects of test animal and human exposures to white phosphorus. It is reported to be one of the most highly toxic inorganic substances (Sullivan 1979). Red phosphorus, on the other hand, is reported in many publications to be relatively harmless unless it contains white phosphorus as an impurity. Reports of adverse health effects of the red allotrope (acute or chronic) are not available (Patty 1981; Wasti 1978). No epidemiological data for red phosphorus are available (Wasti 1978). Animal toxicity data for red phosphorus, however, are available and somewhat clarify the nature of its toxicity. The acute toxicity is characterized by loss of appetite and death. Post-mortem examination revealed extensive fatty degeneration of the liver and kidneys, leukopenia, decrease in the red blood cell count, splenic and genital hyperplasia, and nerve tissue degeneration. Chronic toxicity is characterized by acute parenchymatous or interstitial nephritis, induction of alopecia and desquamation of the skin. The data from these experiments give some insight into the toxicity effects of red phosphorus; however, the information is not complete and does not allow a proper evaluation. No information is available on the absorption, distribution, metabolism or excretion of red phosphorus in humans. No studies have been reported in the literature to determine potential carcinogenic, mutagenic or teratogenic effects of red phosphorus (Wasti 1978).

White phosphorus is a powerful systemic poison. It is absorbed through the skin, by ingestion, and through the respiratory tract. Acute intoxication has resulted generally after oral ingestion of roach poisons containing 1 to 4 percent white phosphorus. The lethal dose (oral ingestion) in adult humans is about 60 mg (1 mg/kg body weight), but as little as 15 mg (0.2 mg/kg body weight) may produce toxic symptoms. Alcoholic beverages may tend to enhance absorption and may be more likely to end the acute toxic phase fatally. Skin contact with white phosphorus produces severe and painful burns, with destruction of the underlying tissue. Absorption through the burned area is probable. Inhalation of white phosphorus vapours has produced tracheobronchitis and liver enlargement. The major characteristic of chronic white phosphorus toxicity is the involvement of bones, especially those of the jaw. The bones become fragile, there is ossification of the growing centers, and widened epiphyseal areas appear. There are also blood and urinary effects. No effects on the liver and the CNS have been observed in chronic poisoning by white phosphorus. There are no reports of cancers induced by white phosphorus in humans; there are no available studies concerning the mutagenic or

teratogenic potential. White phosphorus is metabolized in the body (humans and animals) to phosphate. The site or sites of this oxidation process have not been studied (Wasti 1978).

The oxidation of phosphorus (white and red) has been discussed in detail in other sections of this report. The characteristics of the fumes produced by the combustion of either allotrope are very nearly identical (Steubing 1980; Wasti 1978). The main product of combustion is phosphorus pentoxide (P_4O_{10}) and hydrolysis products thereof. Generally, a concentration of 1000 mg/m^3 in air is intolerable to humans, while the minimum harassing concentration is about 700 mg/m^3. Respiratory distress, nasal discharge, coughing, and soreness and irritation of the throat are characteristic symptoms of exposure. Symptoms of toxicity from test data are also shown in this section.

The toxicological data summarized in this section have been extracted from reliable standard reference sources. Unless indicated otherwise, data refer to white phosphorus exposures. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Both acute (short-term) and chronic (long-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for white phosphorus are based upon its acute effects as conditions causing chronic effects have been largely eliminated. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise. The TLV• of 0.1 mg/m^3 is probably sufficiently low to prevent acute poisoning, but may not provide a wide margin of safety from undesirable effects (Doc. TLV 1981). No standards for red phosphorus have been established (Patty 1981; Wasti 1978).

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV• (8 h)	USA-ACGIH	0.1 mg/m^3	TLV 1983
PEL (8 h)	USA-OSHA	0.1 mg/m^3	NIOSH/OSHA 1981
No standards for red phosphorus dust in air have been established			Patty 1981; Wasti 1978

Guideline (Time)	Origin	Recommended Level	Reference
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	0.3 mg/m^3	TLV 1983
STEL (10 min)	USA-NIOSH	1.5 ppm	AAR 1981
Other Human Toxicities			
IDLH	No data		

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated for white phosphorus as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV•, in ppm)

At 20°C, ITI = 1315.12 x (0.026 mm Hg/0.0194 ppm)
At 20°C, ITI = 1.76×10^3

The ITI is a measure of vapour toxicity and cannot accommodate information pertaining to the toxicity of dusts, solids or aerosols. Therefore no ITI for the combustion fume is presented.

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
25-year-old male, white phosphorus grenade exploded at his feet in Vietman	29% of body burned, urine turned dark, sclerae became icteric, hematocrit and hemoglobin lowered. Urine had only an occasional red cell and there were no hemoglobin casts. Serum calcium was decreased, bilirubin level increased. BUN was elevated and serum albumin depressed. Patient recovered	Wasti 1978

Exposure Level (and Duration)	Effects	Reference
46-year old male, white phosphorus, method of contact unspecified	12.5% of body burned, blood and renal effects persisted despite emergency debridement, cleansing of the wounds and vigorous intravenous fluid administration. Hemodialysis was instituted. Hyperphosphatemia was noted. Patient recovered	Wasti 1978
38-year old female, attempting to extinguish a white phosphorus fire during WW-II	Burns to feet and legs. X-ray examination of the feet revealed a phosphorus-induced bone necrosis particularly in the metatarsals and phalanges with some observable periosteal reaction in both legs	Wasti 1978
SPECIES: Animal		
Rabbit, white phosphorus as 0.1% solution in peanut oil, volume applied and duration not specified	No primary skin irritation observed	Wasti 1978
Rabbit (white, NewZealand), 130 animals, weighed ~3.5 kg each, 10 g of WP onto 7.5 cm area of the back, 1 min duration, residue removed	Effective burn area: 10-20% of total body surface area. Group I - 90 rabbits received no post-burn treatment; 40 rabbits received a total burn excise and closure 1 hour post-burn. Eighty-four of the 130 rabbits died, 75 within 3 days post-burn. No difference in death rate between subgroups. Serum calcium was reduced. Phosphorus elevated in all animals that died. Group II animals received no post-burn treatment. Seventeen of 24 rabbits died. Similar calcium and phosphorus effects observed	Wasti 1978
Guinea pig, white phosphorus, subcutaneous injections of 1 mg/kg body weight at intervals of 3-5 days (total of 7-11 mg)	Increase in number of circulating monocytes	Wasti 1978

Exposure Level (and Duration)	Effects	Reference
SPECIES: Animal		
Unspecified	Liver and kidney damage may result from dermal application	Patty 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	White phosphorus fumes may cause severe ocular irritation with blepharospasm, photophobia, and lacrimation. Particles are caustic and seriously damaging. The cornea was rendered opaque, but interstitial vascularization and episcleritis developed. Episodes of inflammation recurred for many years, but good vision was maintained	TDB (on-line) 1981
Male, age unspecified, encountered spilled white phosphorus	20 min after accident, smoking spots were revealed on the skin of his face and neck. Smoke was emanating from conjunctival sacs. Particles of white phosphorus were embedded in the bulbar and tarsal conjunctivae of his eyes. A slight blepharospasm developed but disappeared within 30 min. 20/20 vision returned 12 h later	Wasti 1978

7.3 Threshold Perception Properties

7.3.1 Odour. No specific odour data for white phosphorus were encountered in the literature. Terms generally used (e.g., mild, characteristic (phossy), garlic-like) describe the odour of the combustion products and possibly phosphine. The red allotrope is odourless.

7.3.2 **Taste.** No data found.

7.4 **Long-term Studies**

7.4.1 **Inhalation** (white phosphorus unless otherwise specified).

Note: Phosphorus generally will ignite on contact with air and form intense white smoke containing primarily phosphorus pentoxide (P_4O_{10}) and hydrolysis products. Asphyxiation can occur in confined areas where the available atmospheric oxygen is consumed during combustion (Sax 1979). Acute white phosphorus intoxication from inhalation has not often been reported; however, the toxic symptoms of a recent instance were weakness, malaise, headache, vertigo, tracheobronchitis, and tender and enlarged livers (Wasti 1978).

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human (5 males)		
35 mg/m^3 white phosphorus and 220 mg/m^3 P_4O_{10} for 2-6 h	Weakness, malaise, headache, vertigo, tracheobronchitis, tender and enlarged livers	Wasti 1978
Greater than 400 mg^3 (10 to 15 min) (white phosphorus vapours or combustion product)	Signs of respiratory tract irritation	Patty 1981
Unspecified (assumed to be combustion products)	Irritation of pulmonary tissues with resultant acute pulmonary edema	USDHEW 1977
Unspecified (assumed to be vapours)	Can cause photophobia with myosis, dilation of pupils, retinal hermorrhage, congestion of the blood vessels and rarely an optic neuritis	Sax 1979
SPECIES: Unspecified		
Unspecified (probably human) (white phosphorus vapours or smoke, usually containing phosphorus pentoxide, 0.035 mg/L)	May produce respiratory tract irritation	Patty 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
500 mg/m^3 (10 min)	LC_{LO}	Wasti 1978
SPECIES: Rabbit		
150-160 mg/m^3 (30 min/d for 60 d)	Decrease in hemoglobin and erythrocyte counts	Wasti 1978
Chronic Exposures		
SPECIES: Human		
(35 years old) Worked in lucifer match factory. Time unspecified	Pain in jaw, ulcerated opening along line of jaw, necrotic jaw	Wasti 1978
Man (35 years old) Packaged white phosphorus for 13 years. Concentration unspecified	Necrosis of the jaw	Wasti 1978
Man (44 years old) Process man on white phosphorus condensers for 10 years. Concentration not specified	Necrosis of upper and lower jaws	Wasti 1978
Man (45 years old) Worked same area as above but for 23 years. Concentration not specified	Right upper jaw necrosis	Wasti 1978
Man (23 years old) Worked for 5 months soldering tins containing white phosphorus	Intense salivation, no necrosis of bone developed probably due to brevity of exposure	Wasti 1978

Note: It has been stated in a review that salivation, ulcerative stomatitis and rapid deterioration of the teeth in a phosphorus factory worker should arouse the suspicion of chronic phosphorus intoxication. Additional symptoms which are pathognomonic of periostitis and incipient necrosis of the jaw bone are dull red spots on the mucous membranes of the oral cavity (Wasti 1978).

7.4.2 Ingestion (white phosphorus unless otherwise specified).

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
16 mg/kg (oral)	TD_{LO}	RTECS 1979
0.2 mg/kg body weight (oral)	Toxic effects may appear	Wasti 1978
2600 µg/kg (oral)	TD_{LO} (Woman)	RTECS 1979
1400 µg/kg (oral)	LD_{LO}	RTECS 1979
1 mg/kg body weight (oral)	Lethal oral dose	Patty 1981; Wasti 1978
4412 µg/kg (red phosphorus)	LD_{LO}	RTECS 1979
Unspecified	After a delay of a few hours, nausea, vomiting and abdominal pain may occur. Symptoms may disappear after 24 to 36 hours, then reappear in a few hours or days, with diarrhea and a yellow colour to the skin. Death may occur	NIOSH/OSHA 1981
Unspecified concentration (toxic doses)	Two stages. Initial stage may include nausea, vomiting, belching within 30 minutes of ingestion. Death from cardiovascular collapse can occur in 12 hours. Period of regression and apparent recovery may occur lasting 2 days. Second stage includes gastrointestinal distress, hepatic, renal and cardiovascular problems, jaundice, pitting edema, oliguria, high pulse rate, low blood pressure	Patty 1981; Wasti 1978

Exposure Level (and Duration)	Effects	Reference
Female (31 years old) 0.19 g white phosphorus in 8 g rat poison (2.7 mg/kg body weight)	Severe epigastric pain, nausea, and vomiting. Refused medical emergency treatment. Symptoms abated on 2nd day. Condition worsened from 4th day on with intensified vomiting, melenous diarrhea, generalized abdominal pain, oligurea, hepatomegaly and pitting edema of the ankles. Gastrointestinal bleeding. Death. Autopsy revealed fatty infiltration of the liver and kidneys	Wasti 1978
Female (16 years old) 15.7 mg/kg body weight	Pulse was 110/min with a systolic pressure of 60 mm Hg. She was cyanotic and manifested poor capillary filling. Atrial fibrillation with wide slurred QRS complexes, diffuse cardiac enlargement. Died of cardiac arrest 22 hours after ingestion. Autopsy showed a pale, dilated heart	Wasti 1978
SPECIES: Rabbit		
7 mg/kg	LD_{LO}	AAR 1981
SPECIES: Mouse		
3.5 mg/kg	LD_{100}	AAR 1981
SPECIES: Rat		
0.5 mg/kg	LD_{100}	AAR 1981
SPECIES: Pig		
160 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Mammal		
200 mg/kg	LD_{LO}	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Rabbit		
0.3 mg/kg body weight/d for 117 d	Reduction in weight gain and retardation of longitudinal bone growth	Wasti 1978
0.2-1 mL of 1% solution of white phosphorus in oil 2-3 times/wk (intravenous) for 15 wk	Nerve degeneration in CNS	Wasti 1978
SPECIES: Rat		
0.0027 mg/kg body weight/d for 25 wk	Slight reduction in weight gain	Wasti 1978
0.0032 mg/kg body weight/d for 22 wk	No ill effects until 15 weeks, after which slight reduction in weight gain	Wasti 1978
0.018-0.07 mg/kg body weight/d for 22 wk	Reduction in weight gain	Wasti 1978
0.01% in cod liver oil for 22-57 d	Reduction in weight gain and retardation of longitudinal bone growth	Wasti 1978
SPECIES: Dog		
0.2-0.8 mg/kg body weight/d for 37 d	Shifts in plasma proteins	Wasti 1978
50 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Guinea pig		
0.75 mg/kg body weight, 4 d/wk for 35 wk	Destruction of hepatic parenchyma	Wasti 1978
SPECIES: Guinea pig and rabbit		
0.6-1 mg/kg body weight/d for 4 mo	Liver cirrhosis	Wasti 1978

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
Acute and Chronic Exposures		
SPECIES: Dog		
2mg/kg	LD_{LO}	RTECS 1979
2 mg/kg	LD_{100}	AAR 1981
0.1 mg/kg body weight/d for 56 d	Hydropic renal degeneration	Wasti 1978
SPECIES: Rabbit		
12.5 mg/kg	LD_{100}	AAR 1981
10 mg/kg	LD_{LO}	RTECS 1979

7.4.4 Exposure to Combustion Products (white phosphorus only). The toxicity data described in this section are for the combustion fume from white phosphorus only; however, the toxicity of the fume from red phosphorus should be similar since the combustion products from either allotrope are essentially the same. No studies for red phosphorus smoke have been reported in the literature. A Mitscherlich test run on the minced carcasses of mice which had been killed with white phosphorus smoke revealed no elemental phosphorus (Wasti 1978).

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
108 subjects (male), 1000 mg/m^3, time not specified	Intolerable, throat irritation and coughing, minimum harassing concentration for men at rest. Unbearable to most people at >1000 mg/m^3	Wasti 1978

Exposure Level (and Duration)	Effects	Reference
108 subjects (male), 700 mg/m^3, time not specified	Minimum harassing concentration for men at work	Wasti 1978
Number of subjects not specified, presumed to be male, 592-588 mg/m^3 for 3.5 min and 2 min, respectively	Respiratory distress, nasal discharge, coughing, throat irritation and soreness	Wasti 1978
7 subjects (male), 514 mg/m^3 for 16 min	Nose and throat irritation, coughing during exposure, 3 subjects had no effects during the 6 days post exposure	Wasti 1978
6 subjects (male), 453 mg/m^3 for 10 min	5 of 6 subjects showed throat irritation. One of the 5 experienced nausea and nasal discharge during 3 days post exposure	Wasti 1978
6 subjects (male), 425 mg/m^3 for 15 min	Nose and throat irritation during exposure but no remarkable effects during 3 days post exposure	Wasti 1978
5 subjects (male), 408 mg/m^3 for 10 min	4 of 5 subjects had throat irritation and coughing. One subject experienced sore throat and symptoms of cold during 3 days post exposure	Wasti 1978
7 subjects (male), 188 mg/m^3 for 5 min	5 of 7 experienced throat irritation, coughing and slight headache during exposure. 24 hours later, 4 subjects had frontal headache, nasal congestion, throat irritation and coughing. After 2 and 3 days, only one subject showed signs of respiration irritation	Wasti 1978

Note: Animal (mice, rats, goats) data are available (Wasti 1978) but are not included as they did not appear to contribute to the understanding of human data.

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of mucous membranes of nose, throat, and respiratory tract.
2. Cough.
3. Dilation of pupils (Sax 1968).
4. Photophobia with myosis (Sax 1968).
5. Congestion of blood vessels (Sax 1968).
6. Retinal hemorrhage (Sax 1968).
7. Phosphorus necrosis of the jaw ("phossy jaw").
8. Bronchitis.
9. Pneumonia.
10. Acute pulmonary edema (USDHEW 1977).
11. Asphyxiation (USDHEW 1977).
12. Enlarged livers (Wasti 1978).
13. Weakness (Wasti 1978).
14. Malaise (Wasti 1978).
15. Headache (Wasti 1978).
16. Vertigo (Wasti 1978).
17. Intense salivation (chronic) (Wasti 1978).
18. Ulcerative stomatitis (chronic) (Wasti 1978).
19. Rapid deterioration of teeth (chronic) (Wasti 1978).
20. Bone necrosis (jaw) (chronic) (Wasti 1978).
21. Dull red spots on mucous membranes of oral cavity (chronic) (Wasti 1978).

7.5.2 Ingestion. Symptoms due to ingestion of white phosphorus may be delayed for periods of a few hours to 3 days (CHRIS 1978).

1. Garlic odour of the breath.
2. Nausea, vomiting.
3. Abdominal pain (CHRIS 1978).
4. Depression (CHRIS 1978).
5. Yellow skin colour (NIOSH/OSHA 1981).
6. Diarrhea (NIOSH/OSHA 1981).
7. Delirium (CHRIS 1978).
8. Low blood pressure (CHRIS 1978).
9. Hemorrhage (Goodman 1980).

10. Hepatic necrosis (Goodman 1980).
11. Coma (CHRIS 1978).
12. Cardiovascular failure (Goodman 1980).
13. Death (Goodman 1980).

7.5.3 Skin Contact.

1. Severe burns.
2. Blistering.
3. Skin turns greyish white.
4. Infection may ensue.
5. Lowered hematocrit and hemoglobin (Wasti 1978).
6. Serum calcium decreased (Wasti 1978).
7. Bilirubin level increased (Wasti 1978).
8. Serum albumin depressed (Wasti 1978).
9. Renal effects (Wasti 1978).
10. Blood effects (Wasti 1978).
11. Hyperphosphatemia noted (Wasti 1978).
12. Bone necrosis.

7.5.4 Eye Contact.

1. Ocular irritation.
2. Lacrimation.
3. Blepharospasm (TDB (on-line) 1981; Wasti 1978).
4. Photophobia.
5. Conjunctivitis with a yellow tint (Sax 1968).
6. Severe burns.
7. Permanent damage.

7.5.5 Summary of Symptomology. Acute poisoning symptoms generally occur in three stages:

First stage - symptoms due to local irritation occur within a few minutes or hours after exposure and last from 8 hours to 3 days. Effects are not immediate except for thermal burns on body surface. Skin contact results in painful, penetrating, second and third degree burns which heal slowly. Both chemical and thermal damage is inflicted. Ingestion produces a sensation of warmth or a burning pain in the throat and abdomen, with intense thirst. Nausea, vomiting, diarrhea and severe pain are typical. A garlic

odour from breath and excreta is highly suggestive of phosphorus ingestion. Luminescent vomitus and feces are essentially diagnostic of phosphorus. Shock may be of such severity as to cause death in 24 to 48 hours.

Second stage - this may be an almost symptom-free period lasting from 8 hours to several weeks. The patient may appear to be recovering.

Third stage - this stage is typified by symptoms of systemic toxicity from an absorbed poison. Nausea, protracted vomiting, diarrhea and massive hematemesis may occur. Other symptoms include liver tenderness and enlargement, jaundice, and pruritus. Also, hemorrhages into skin, mucous membranes and viscera may occur, due to injury of blood vessels and inhibition of blood clotting. Renal damage is evidenced by oliguria, hematuria, casts, albuminuria and sometimes anuria. Cardiovascular collapse may occur due to a direct toxic action of phosphorus on the heart muscle and blood vessels. This usually occurs late in the course of the poisoning. The central nervous system may be involved resulting in convulsions, delirium and coma. Cerebral symptoms may persist for a long time if the victim survives this stage. Finally, death usually occurs in 4 to 8 days, but may be delayed for 3 weeks. Irreversible shock, hepatic failure, central nervous system damage, massive hematemesis or renal insufficiency may be the proximal cause of death.

Chronic poisoning from ingestion or inhalation is characterized by cachexia, anemia, bronchitis, general debility and necrosis of the mandible. These are all associated with lowered resistance to infection and defective tissue repair (Gosselin 1976).

7.6 Human Toxicity to Decay or Combustion Products

Even though the combustion of phosphorus (white or red) results in a fume cloud more complex in nature than usually postulated, two of the primary products are phosphorus pentoxide (P_4O_{10}) and phosphorus trioxide (P_4O_6). Both molecules are highly irritating to skin, mucous membranes and eyes; both have a strong affinity for water. The former readily absorbs moisture from the air. Since both molecules are the anhydrides of phosphoric (H_3PO_4) and phosphorous acids (H_3PO_3), the acids will be the ultimate products of the reactions with water; the contaminated air surrounding a phosphorus fire will therefore be acidic. It is pointed out, though, that the reaction of the components of the cloud with water from the air and firefighting is also complicated and many intermediate products will be present. The final product from the reaction with excess water will be orthophosphoric acid (H_3PO_4). This compound is also an irritant to the skin and eyes. Under certain conditions, phosphine (PH_3) may be formed. For example,

phosphorus trioxide reacts violently with hot water to produce phosphine; phosphorous acid, if present at all, also thermally decomposes to produce phosphine. Both compounds will readily be converted to the pentoxide and phosphoric acid, respectively, in the presence of excess oxygen from the air. Emergency response personnel should always be in full protective clothing and wearing a self-contained breathing apparatus when fighting a phosphorus fire (Merck 1983; Sax 1979; Meyer 1977; Cotton 1972; Hawley 1977). Specific toxicity data are discussed in Section 7.4.4. There is no evidence for the presence of unreacted phosphorus in the fume cloud. This is based on animal data (Wasti 1978).

White phosphorus will ignite spontaneously when exposed to air, generating intense, irritating smoke. It emits highly toxic oxides of phosphorus (Sax 1968). When white phosphorus burns in a free supply of air, phosphorus pentoxide is formed (Partington 1958). Asphyxiation can occur in confined areas where the oxygen is consumed upon ignition.

Both phosphorus pentoxide and trioxide, and orthophosphoric acid are highly irritating to skin, eyes and mucous membranes. Inhalation of the fumes from burning phosphorus, which contain at a minimum both of the above oxides and initial hydrolysis products, can lead to serious lung injury (when the oxides dissolve in the liquid within the lung and assorted passages forming various phosphorus oxyacids). Some of the better known oxyacids (e.g., meta, pyro- and polyphosphoric acid) are known to be irritants and moderately toxic. Both of the above oxides react vigorously with water to produce heat; in some cases, the reaction may be violent, with the formation of phosphine. The latter has a disagreeable, garlic-like odour and has a TLV-TWA of 0.4 mg/m^3 and a TLV-STEL of 1 mg/m^3. The corresponding values for orthophosphoric acid are 1 and 3 mg/m^3, respectively. No TLV values have been established for the pent- and trioxides or the less characterized lower oxides (PO_x). Phosphine causes pain in the region of the diaphragm and a feeling of coldness. In general, symptoms of exposure may be weakness, vertigo, dyspnea, bronchitis, edema, lung damage, convulsions, coma and death (Merck 1983; Sax 1979; Meyer 1977; Hawley 1977).

8 CHEMICAL COMPATIBILITY

The specific allotrope is noted if specified in the given reference; otherwise, no allotropic specification is indicated. In some cases, the nature of the reaction conditions gives a clue to the identity of the allotrope.

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	OF GREATER TOXICITY	PRESSURIZATION OF SUBSTANCES	VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Heat (white, red)		•													Sax 1979
Fire (white, red)		•													Sax 1979
Friction (red)		•									•				Bretherick 1979
Air (white)	•	•				•								Ignites spontaneously in air	NFPA 1978
SPECIAL CHEMICALS															
Ammonium Nitrate (white)		•												Ignites in molten salt and with percussion	Bretherick 1979; NFPA 1978
Antimony Pentafluoride		•												On contact	NFPA 1978; Bretherick 1979
Beryllium		•												Incandescent when heated	NFPA 1978; Bretherick 1979
Boron Triiodide (white, red)		•												With incandescence	NFPA 1978; Bretherick 1979

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Bromine (gas) (white)	•												On contact	Bretherick 1979
Bromine (liq.) (white)		•												Bretherick 1979
Bromine (liq.) (red)	•													Bretherick 1979
Bromine Pentafluoride (red)	•									•			Reaction violent on contact at ambient or slightly elevated temperature; ignition often occurs	Bretherick 1979
Bromine Trifluoride	•												Incandescence on contact	Bretherick 1979
Calcium Hydroxide (hot)	•												On contact evolves PH_3 which usually ignites	Bretherick 1979
Cerium										•			At 400-500°C	NFPA 1978; Bretherick 1979
Cesium	•									•			Vigorous reaction below 250°C	NFPA 1978
Cesium Carbide (Di) (Implies CsC_2)										•			Postulated	Bretherick 1979

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Cesium Carbide (Mono) (Implies $CsHC_2$)		•											Incandescent when warmed in contact with phosphorus	NFPA 1978; Bretherick 1979
Cesium Nitride	•												Readily attacked by phosphorus	NFPA 1978
Charcoal		•											When sprinkled with animal charcoal, ignites at 15.5°C in air	NFPA 1978
Chlorine (white, red)		•											On contact	Bretherick 1979
Chlorine (liq.) (white)			•										On contact	Bretherick 1979
Chlorine Dioxide (ClO_2)		•	•										Spontaneous ignition, may explode	NFPA 1978; Bretherick 1979
Chlorine Monoxide (Cl_2O)			•							•			On contact	NFPA 1978
Dichlorine Hexoxide (Cl_2O_6) (white)			•											NFPA 1978
Chlorine Trifluoride		•											Vigorous reaction	NFPA 1978

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Chlorosulphonic Acid ($ClSO_2OH$) (white)			•							•			Vigorous reaction at 25-30°C, end with explosion	NFPA 1978; Bretherick 1979
Chlorosulphuric Acid (SO_2Cl_2) (red)			•							•			Same as above, but high initial temperature	NFPA 1978; Bretherick 1979
Chromium Trioxide (white)			•										With molten oxide at 200°C	NFPA 1978; Bretherick 1979
Chromyl Chloride (CrO_2Cl_2)			•										Explodes with moistened phosphorus	NFPA 1978; Bretherick 1979
Copper		•											When mixture is heated	NFPA 1978; Bretherick 1979
Copper Oxide (I or II) (red)										•			Vigorous reaction on heating	Bretherick 1979
Cyanogen Iodide (ICN)		•											Incandescent with molten phosphorus	NFPA 1978; Bretherick 1979
Fluorine (white, red)		•											On contact	NFPA 1978; Bretherick 1979
Hexalithium Disilicide		•											Incandescent	Bretherick 1979

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Hydriodic Acid (red)			•										Potential for explosion when when mixture used as reducing agent	Bretherick 1979
Hydrogen Peroxide (white, red)		•								•			If phosphorus not completely immersed, heating at solution/air interface can cause ignition, concentrated H_2O_2 >30%	Bretherick 1979
Iodine (white)		•											On contact, room temperature	Bretherick 1979; NFPA 1978
Iodine Monobromide										•			With molten IBr	NFPA 1978
Iodine Monochloride										•			With molten ICI	NFPA 1978
Iodine Pentafluoride (red)		•											Spontaneous with incandescence	NFPA 1978; Bretherick 1979
Iodine Trichloride		•											On contact	Bretherick 1979
Iron		•											Mixture can become incandescent when heated	NFPA 1978

8.1 **Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups** (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Lanthanum										•			At 400-500°C	NFPA 1978; Bretherick 1979
Lead Dioxide (PbO_2) (white)		•											On contact	NFPA 1978; Bretherick 1979
Lead Dioxide (PbO_2) (red)	•												On contact	NFPA 1978; Bretherick 1979
Lead Monoxide (PbO) (red)	•												With grinding or warming	Bretherick 1979
Lithium										•			With strongly heated phosphorus	NFPA 1978;
Lithium Carbide (di) (Li_2C_2)	•												Burn vigorously in phosphorus vapour	Bretherick 1979
Lithium Silicide (Li_6Si_2)	•												With incandescence	NFPA 1978
Magnesium Perchlorate		•											Upon mixing, probably due to presence of anhydrous perchloric acid	NFPA 1978; Bretherick 1979
Manganese	•												Upon heating	NFPA 1978; Bretherick 1979

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Manganese Dioxide (red)										•			Vigorous reaction upon heating	Bretherick 1979
Mercuric Oxide		•											When mixture is struck with a hammer and when boiled with water and phosphorus	NFPA 1978
Mercury Oxide (I or II) (red)	•												On grinding or warming, ignition may occur	Bretherick 1979
Mercurous Nitrate (White)		•											On impact	NFPA 1978; Bretherick 1979
Neodymium										•			Above 400°C	NFPA 1978; Bretherick 1979
Nickel	•												Mixture can become incandescent when heated	NFPA 1978
Nitric Acid	•												Ignites in HNO_3 vapour and burns with intense white light	NFPA 1978

8.1 **Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups** (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Nitrogen Dioxide (N_2O) (white)	•												Warm or molten	NFPA 1978; Bretherick 1979
Nitrogen Oxide (NO or N_2O) (white)	•												Warm or molten	Bretherick 1979
Nitrogen Pentaoxide (N_2O_5) (white)	•												Warm or molten	Bretherick 1979
Nitrogen (Tri)-bromide		•								•			On contact	NFPA 1978
Nitrogen Tribromide Hexaamomoniate		•											Violent explosion on contact	Bretherick 1979
Nitrogen Trichloride		•											On contact	NFPA 1978
Nitrosyl Fluoride	•												With incandescence	NFPA 1978; Bretherick 1979
Nitryl Fluoride (FNO_2) (red)	•												Reacts at room temperature	NFPA 1978; Bretherick 1979
Osmium	•												Incandesces in phosphorus vapour	Bretherick 1979

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Oxygen (white)	•												Readily ignites	NFPA 1978; Bretherick 1979
Oxygen Difluoride (F_2O) (red)	•												Ignites when gently warmed on contact	Bretherick 1979
Trioxygen Difluoride (F_2O_3) (red)	•	•											Ignition and/or mild explosion with single drops of F_2O_3 at -183°C	Bretherick 1979
Performic Acid (CH_2O_3) (red)										•			Violent oxidation	NFPA 1978; Bretherick 1979
Platinum	•												Burns vividly below red heat	Bretherick 1979; NFPA 1978
Potassium										•			Vigorous reaction below 250°C	NFPA 1978
Potassium (di) Carbide (K_2C_2)	•									•			Postulated to be violent	Bretherick 1979
Potassium Hydroxide	•												When boiled with an aqueous KOH solution, PH_3 evolved (also P_2H_4 which is spontaneously flammable; PH_3 is not)	NFPA 1978; Bretherick 1979

8.1 **Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups** (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Potassium Iodate (white, red)			•							•			With addition of a little water to mixture	Bretherick 1979
Potassium Nitrate (red)										•			Oxidizes vigorously when heated with KNO_3	Bretherick 1979
Potassium Nitride		•											Produces highly flammable mixture which evolves NH_3 and PH_3 with water	NFPA 1978; Bretherick 1979
Potassium Permanganate			•							•			Upon grinding mixture, more violent if also heated	NFPA 1978; Bretherick 1979
Potassium Peroxide (K_2O_2) (white)			•										On contact	Bretherick 1979
Potassium Peroxide (red)			•										On contact	Bretherick 1979
Praseodymium										•			Above 400°C	Bretherick 1979
Rubidium										•			Vigorous reaction below 250°C	NFPA 1978

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Rubidium Carbide ($RbHC_2$)		•											Becomes incandescent when in contact with phosphorus	NFPA 1978; Bretherick 1979
Rubidium (di) Carbide (Rb_2C_2)										•			Postulated to be violent	Bretherick 1979
Selenium		•											Attains incandescence	Bretherick 1979
Selenium Monochloride (Se_2Cl_2)			•										When mixed	NFPA 1978
Selenium Oxychloride ($SeOCl_2$) (white)			•											NFPA 1978; Bretherick 1979
Selenium Oxychloride (Red)		•											Incandesces	NFPA 1978; Bretherrick 1979
Selenium Oxyfluoride		•											Ignites spontaneously	NFPA 1978; Bretherick 1979
Selenium Tetrafluoride										•				NFPA 1978; Bretherick 1979
Silver Nitrate (white)			•										On impact	NFPA 1978; Bretherick 1979
Silver Oxide (AgO) (red, amorph.)		•											Upon grinding or warming	NFPA 1978; Bretherick 1979

8.1 **Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups** (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sodium										•			Vigorous reaction below 250°C	NFPA 1978
Sodium Carbide (Na_2C_2)		•											Burns vigorously in phosphorus vapour	NFPA 1978; Bretherick 1979
Sodium Chlorite (NaOC1) (red)	•									•			Reaction can have a sudden, almost explosive stage - In aqueous suspension	NFPA 1978; Bretherick 1979
Sodium Hydroxide		•											See Potassium Hydroxide	NFPA 1978; Bretherick 1979
Sodium Peroxide (Na_2O_2) (white)			•										On contact	NFPA 1978; Bretherick 1979
Sodium Peroxide (red)		•											On contact	NFPA 1978; Bretherick 1979
Sulphur (S_8) (white)		•	•										When warmed, combusts and explodes	NFPA 1978

8.1 Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sulphur Trioxide (SO_3) (gas) (white)		•											Ignites after exposure to SO_3 vapour, some delay on contact with SO_3 (l)	NFPA 1978; Bretherick 1979
Sulphur Trioxide (liq.) (white)		•								•			Large pieces cause ignition	NFPA 1978; Bretherick 1979
Sulphuric Acid (H_2SO_4) (white)		•											Ignites on contact with boiling concentrated H_2SO_4	NFPA 1978; Bretherick 1979
Sulphuryl Chloride (red)										•			Vigorous reaction on warming	Bretherick 1979
Disulphuryl Chloride (red)										•			Vigorous reaction on warming	Bretherick 1979
Disulphur Dibromide (S_2Br_2) (red)										•			Violent reaction	Bretherick 1979
Thorium		•											Incandescent when heated	NFPA 1978; Bretherick 1979
Vanadium Oxytrichloride			•										Mixture explodes below 100°C with more than small amounts	NFPA 1978

8.1 **Compatibility of Phosphorus (White, Red) with Other Chemicals and Chemical Groups** (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Zirconium		•											Incendescent when heated in a vacuum	NFPA 1978; Bretherick 1979
CHEMICAL GROUPS														
Alkalies (Hydroxides)		•											Contact with caustic alkalies evolves mixed phosphines which usually ignite in air	NFPA 1978; Bretherick 1979
Halogens Azides (white)			•										Explode violently on contact, XN_3 where X = Br, Cl, I	Bretherick 1979
Metal Halogenates (white, red)			•										Ba, Ca, Mg, K, Na, Zn explode on initiation by friction, impact or heat with finely divided, dry phosphorus	Bretherick 1979
Oxidizing Agents (white, red)			•						•					EPA 600/ 2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following comments and/or procedures have been gleaned from the literature and are reviewed or mentioned throughout this manual. In some cases, the wording of the original source has been extracted verbatim. In other cases, the wording has been changed to ensure the flow of the section or subsection is smooth, while hopefully not changing the meaning of the data. The following paragraphs will include comments and procedures that should not be considered the recommendations of Environment Canada. Unless it is felt necessary, no references will be given in this section.

9.1.1 Fire Concerns. White phosphorus is classified as a spontaneously combustible solid while the red allotrope is classified as a flammable solid. The latter can be ignited by friction or sparks; due to a very slow exothermic reaction with atmospheric water vapour and oxygen, spontaneous combustion may result if large quantities are stored in piles. The latter reaction is accelerated by an increase in temperature. As mentioned above, white phosphorus (solid, liquid or gas) is spontaneously flammable on contact with air. The heat generated during combustion of a solid mass will eventually lead to melting and flowing of the burning liquid. The combustion of the white or red allotrope produces a voluminous cloud of particulate oxides and hydrolysis products. It is stated that the smokes from either source are almost identical; that of the white allotrope seems to be denser (Wasti 1978). The combustion of phosphorus in a closed space will lead to rapid oxygen depletion. Contact with strong caustics will produce phosphine gas. The latter is extremely toxic and flammable, although not spontaneously unless mixed with biphosphine (P_2H_4) impurity. A review of Section 8 is recommended at this point. Protective clothing and self-contained breathing apparatus are mandatory equipment when involved in a phosphorus-related emergency.

9.1.2 Fire Extinguishing Agents. A phosphorus (white or red) fire can be controlled with water, sand or similar materials which will exclude air. The main objective is to solidify any molten phosphorus and maintain a water film on the resulting solid. To accomplish this, steady, low-pressure volumes of water are generally required. High-pressure, direct streams of water can spread molten phosphorus and increase the area of fire. It may be necessary to dam or seal the fire area where a large quantity of phosphorus is involved; the burning substance can be submerged under water. Soil, sand

bags, etc., can be used for this purpose. For small fires, water, wet sand or earth, or foam may be used effectively. Dry chemical is not effective. Large fires will generally require water spray. Cool fire-exposed containers with water; remove from fire area if this can be accomplished without risk.

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation. Full firefighters protective clothing and self-contained breathing apparatus should be worn. If a leak occurs in a small container or a tank container, it can best be controlled at the source by applying a steady stream of water to the wall of the container at the leak site. The water will reduce the temperature of the liquid phosphorus and convert it to the solid form, effectively plugging the leak.

9.1.3.2 Spills on land. A spill of solid or molten white phosphorus on land will usually result in ignition. At atmospheric pressure, however, ignition may not occur at temperatures approaching 0°C or below. Whether or not ignition has occurred, contain, if possible, by forming a mechanical barrier with sand, soil, or sand bags to prevent spreading of the molten substance or fire area. Cover spill area with wet sand or water and carefully shovel into water-filled containers equipped with airtight covers for recovery or disposal. It is recommended that the sand be kept wet by water spray. Water from precipitation, firefighting or fire prevention should be contained for decontamination on site or transported to a decontamination facility. Aeration is effective for oxidation of white phosphorus in water (phossy water) but ozonation is faster and more effective (Campbell 1977). Aeration and ozonation are compared in Figure 8.

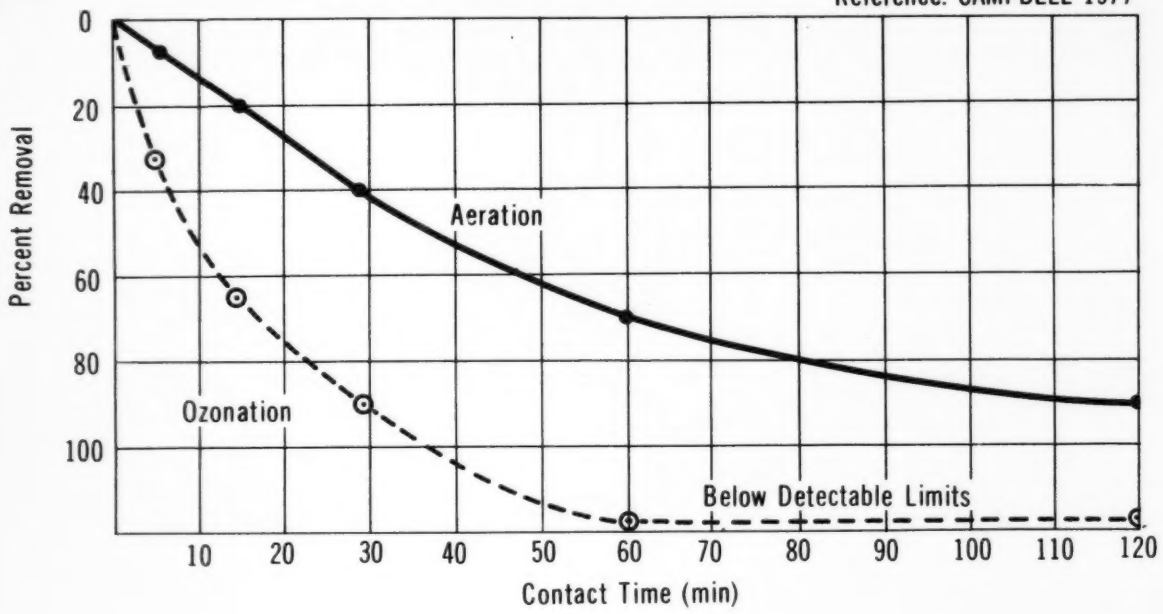
9.1.3.3 Spills in water. Contain if possible by forming deep natural water pockets or using sand bag barriers to trap material at the bottom. Remove trapped material, if still in liquid form, with suction hoses and place in water-filled containers. Solid may be mechanically removed with care and placed in similar containers. Every effort should be made to remove the undissolved mass. If the spilled material cannot be recovered immediately, the following cover materials are recommended to oxidize phosphorus <u>in situ</u>: sulphur, pyrites and solid oxidizing agents (CG-D-56-78). The surrounding water should be checked for phosphorus contamination and treated accordingly (see Section 9.1.3.2).

FIGURE 8

PHOSPHORUS

COMPARISON OF AERATION WITH OZONATION AS A MEANS TO OXIDIZE WHITE PHOSPHORUS IN WATER

Reference: CAMPBELL 1977



OZONATION:	**% Removal**	**35**	**65**	**90**	**98**	**98**
	Time	**5**	**15**	**29.5**	**60**	**120**
AERATION:	**% Removal**	**9**	**20**	**40**	**70**	**90**
	Time	**5**	**15**	**29.5**	**60**	**120**

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills in water. As mentioned in Section 9.1.3.3, the spilled mass, whether solid or liquid, should be trapped by whatever means possible and removed mechanically or by suction if still molten. The recovered mass must be stored under water at a temporary site on land or in containers. Eventual transfer to water-filled containers is mandatory for transfer to a disposal or recovery site. The contaminated water body and the water displaced from the temporary land storage site or containers must also be decontaminated (see Section 9.1.3.2).

9.1.5 Disposal. Waste phosphorus (white or red) or contaminated water (phossy water) must never be discharged directly into sewers or surface waters. The former may

be incinerated under careful supervision, with equipment designed to handle the oxides of phosphorus combustion products. The latter can be effectively decontaminated by ozonation (Figure 8) (Campbell 1977). Following treatment, either at the spill site or at a waste management facility, the resultant sludge, if any, can be disposed of to a secure landfill.

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics and unknown, self-contained breathing apparatus and a totally encapsulated chemical or firefighting suit should be worn.

If the spilled material is known to be white phosphorus:

- Response personnel should be provided with and required to use flame-retardant clothing, gloves, face shields (20 cm minimum) and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid white phosphorus (NIOSH/OSHA 1981).
- Dust and splash-proof safety goggles are also recommended for eye protection (NIOSH/OSHA 1981).
- Neoprene and rubber are recommended for suits, gloves and boots (Mobil MSDB 1979).
- Any clothing which becomes contaminated with white phosphorus should be removed immediately and not reworn until the phosphorus is removed from the clothing (NIOSH/OSHA 1981).
- Eyewash stations and chemical safety shower should be readily available in areas of use or spill situations (GE 1977).
- Self-contained breathing apparatus should be used or immediately available for use in areas of handling or use. SCBA should be worn in any emergency situation.

The following is a list of the minimum respiratory protection recommended for personnel working in areas where white phosphorus is present (NIOSH/OSHA 1981):

Condition	Minimum Respiratory Protection* Required above 0.1 mg/m^3
Particulate Concentration 5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
200 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.

Condition	Minimum Respiratory Protection* Required above 0.1 mg/m^3
Greater than 200 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

* Only NIOSH-approved or MSHA-approved equipment should be used.

9.1.7 Special Precautions.

9.1.7.1 White phosphorus. White phosphorus is spontaneously flammable on contact with air and as a result is stored under water. Since it will react with dissolved oxygen to form phosphoric acid, the normally recommended material of construction is 316 stainless steel. The water cover must be sufficient to ensure that the substance is never exposed to air. During cooling and solidification, the solid will contract and pull away from the container wall allowing the water level to drop. All containers should be transported and stored in an upright position. They must be allowed free movement on the carrying vehicle to prevent physical damage to the containers. Bulk shipments are loaded molten and usually stay mostly molten due to outside insulation and the insulating ability of phosphorus. Small containers are loaded in the liquid state, but should solidify in a fairly short time. Rupture of a small container (drum) results in loss of water, exposure to air, and usually ignition of the phosphorus. Containers of white phosphorus, drum-type or smaller, should be stored in a cool, dry and well-ventilated place. They should be kept away from flammable, combustible materials and oxidizing agents (see Section 8). Containers should be frequently checked for corrosion and leaks. Wherever containers of white phosphorus are handled or stored, adequate supplies of water should be readily available. Manufacturers and handlers of bulk quantities of white phosphorus should be contacted for specifics regarding special precautions, although the above comments should generally apply (Wasti 1978).

9.1.7.2 Red phosphorus. Red phosphorus is stored in air-tight steel containers in the dry state. All comments regarding transport and storage conditions for white phosphorus should generally apply to this allotrope. Specifically, physical damage to the container that could result in ignition by friction, spark or impact must be avoided. Chemical compatibility must be ensured. An adequate water supply for firefighting purposes must be readily available.

10 PREVIOUS SPILL EXPERIENCE

10.1 General

A number of spill incidents for this chemical have been documented. The incident discussed below was selected primarily because significant information, potentially useful in future spill circumstances, has been obtained from it.

10.2 White Phosphorus Fire (Lafornara 1980)

The following incident occurred in Gettysburg, PA, in early 1979 and involved a tractor-trailer containing 89-90 drums of white phosphorus. The seals or liners of all the drums were broken and the contents of many consumed during the fire that lasted for several hours. This incident is thought appropriate for this manual because the sequence of events is well documented and involves not only data concerning the initial incident and cleanup, but also data related to problems that were encountered as a result of heat generated by the fire. The details are not presented in the sequence that they appear in the reference; the authors have taken the liberty to insert other referenced data or personal comments where deemed appropriate. These inserts will be individually referenced and/or bracketed.

At 2:15 a.m. on March 22, 1979, a tractor-trailer en route from Fort Pierce, FL, to West Chester, PA, with 89 (or 90) 30-gallon drums of white phosphorus caught fire in Gettysburg, PA. The fire was extinguished by the local fire fighters after several hours by burying the entire tractor-trailer rig with wet sand. During the time they were fighting the fire, explosions occurred and voluminous, irritating fumes were emitted into the atmosphere. As a result, local police and fire authorities had evacuated 100 persons from the immediate vicinity. More than 100 persons, including 9 civilians and numerous fire fighters, were hospitalized with respiratory symptoms from inhaling the fumes. (As stated in Section 9.1.6, standard respiratory protection for personnel involved in fire-fighting is a self-contained breathing apparatus. Use of this equipment will minimize or eliminate inhalation of toxic or irritating fumes and thereby reduce incident-related injuries.)

The cleanup operation consisted of removing the individual drums from the sand and packing each one in a 55-gallon drum which was then filled with water. This operation was assisted by a team of experts from the manufacturer of the phosphorus. The 86 55-gallon drums containing 33 000 lbs. of white phosphorus were then loaded onto two trailers and taken to the truckers terminal in Hagerstown, MD, for temporary

storage. The remainder of the sand and solid debris, which was only slightly contaminated, was trucked to an approved waste disposal site.

As mentioned earlier, all of the 30-gallon drums in the shipment were exposed to extreme heat during the trailer fire. After the fire was extinguished, it was found that 11 drums were completely empty and the remainder damaged to varying degrees. Some had lids that were burst open, some drums has swollen, and all had their neoprene gaskets burned or melted away. It was at this time that the manufacturer's response personnel recommended that the drums would have to be overpacked by 55-gallon drums filled with water. This was accomplished using a front-end loader and a sling. Each smaller, damaged drum was lifted into a 55-gallon container which was then filled with water, covered, sealed and placed in one of the two trailers for transport (presumably back to Mulberry, FL, where the phosphorus was produced). After the overpacking was completed, the two trailers returned to the truckers terminal with their load. It was later reported to EPA and State of Maryland personnel that during the overpacking process, many of the drums were heard to pop internally, and that one drum had actually exploded, injuring 6 people (the nature of their injuries was not mentioned). In addition to the late report immediately above, it was also reported by various personnel who were on-scene at Gettysburg that they had detected the garlic-like odour usually associated with phosphine. Another fact to keep in mind is that the white phosphorus was shipped in and still remained in its original steel drum, now overpacked with another steel drum, and the original water, if any remained after the fire, still in the drum.

The internal popping and the explosion cannot be explained by the mere presence of white phosphorus in the drums. It can only be explained if some or all of the phosphorus had reacted to form explosive gases. This is possible if (as is likely) the following sequence of events and resulting chemical reactions took place:

1. The seals melted or burst during the fire. The heat more than likely caused some of the water to evaporate, thereby air to enter the drums on cooling.
2. The air contacted exposed white phosphorus and reacted with it to form combustion products, generally phosphorus pentoxide (P_4O_{10}). (However, in this case oxygen may have been in demand and lower oxides were no doubt also formed.)
3. The phosphorus pentoxide (and others) dissolved in the remaining water to form phosphoric acid (H_3PO_4) and possibly other oxyacids, e.g., phosphorous acid (H_3PO_3), which is not thermally stable, decomposing to phosphoric acid and phosphine (Cotton 1972).
4. The acid reacted with the steel drum to form metal salts and hydrogen (an explosive gas).

An alternative reaction could have been a direct interaction of white phosphorus and hot water producing phosphine in addition to forming hydrogen. Hydrogen is a strong reducing agent and can react with either phosphoric acid or white phosphorus to produce phosphine. Since the phosphine characteristic odour was detected at the incident site, it seems quite probable that it was being generated by one of the mechanisms presented. Also, it is possible the reaction sequence was still proceeding and would continue as long as the phosphorus and the original water remained in steel drums.

The chemistry and properties of phosphorus and its oxyacids have been presented throughout this manual. Some additional words concerning the chemistry aspect are thought worthwhile at this point. Both orthophosphoric (H_3PO_4) and phosphorous acids (H_3PO_3) are considered moderately strong with pHs of 2.15 and 1.8 for their respective first protons. The chemistry of their dilute solutions is much the same as for other strong acids, namely, they undergo neutralization with caustics, attack most metals to form orthophosphates or phosphites and generate hydrogen gas in the process (Lafornara 1980). And as mentioned earlier, phosphorus acid decomposes to phosphoric acid and phosphine. The latter can also be formed by the reaction of the acids with strong reducing agents like hydrogen.

In the absence of catalysts, temperatures greater than 280°C are required for the oxidation of white phosphorus by water. Under these conditions, the reaction is rapid:

$$P_4 + 6H_2O \rightarrow 2HPO(OH)_2 + 2PH_3 \uparrow$$

Catalysts accelerate this oxidation reaction. They include salts of transition metals, such as iron from oxidized steel, and phosphoric acid itself. The latter seems to act catalytically as the rate of oxidation of white phosphorus accelerates as this product is formed. A sequence of partial reactions that may accompany the above reaction is

$$HPO(OH)_2 + H_2O \rightarrow OP(OH)_3 + H_2 \uparrow$$

and

$$PH_3 + 4H_2O \rightarrow OP(OH)_3 + 4H_2 \uparrow$$

When the above sequence of reactions runs to completion, only phosphoric acid and hydrogen are found. Insufficient water will lead to condensed phosphoric acids in lieu of the ortho species.

Normally, white phosphorus vapour will not react with hydrogen; however, it has been shown to react under pressure at 360°C to form phosphine (Van Wazer 1958).

The conditions may have been right in the drums during the fire to have facilitated any or all of the reaction schemes presented above. Certainly there was evidence for the presence of phosphine and possibly for hydrogen.

A sequence of events following arrival and storage of the drums at the terminal took place that led to the final disposal of the drums by detonation by a U.S. Army Explosive Ordnance Disposal (EOD) Team at a remote site. The manufacturer abandoned the shipment because of the presence of apparent explosive and toxic gases in the drums. The degree of hazard to the local populace around the temporary storage was evaluated by the manufacturers' representatives and state and federal environmental officials. The risk was found to be high and it was decided by the National Response Team to dispose of the drums at a remote site on Fort A.P. Hill, VA. The trucks containing the drums were moved to the site in a 22-vehicle convoy which consisted of fire and water trucks, dump trucks containing a total of 200 tons of sand, low-boys carrying bulldozers, and response team vehicles from EPA, the Maryland Department of Natural Resources, the EOD team, and O.H. Materials, Inc. The detonation of the 86 drums took 12 days to complete.

The above risk assessment was accomplished by considering the principal hazards associated with the situation. These were 1) the potential release of phosphine, an extremely toxic gas, 2) the potential explosion of the hydrogen/phosphine mixture within the drums and 3) the release of a fume cloud of combustion products. A less apparent hazard was the potential for release of the phossy water within each drum. It was deemed apparent that the drums were corroding from within and could conceivably begin to leak the contaminated water at any time. The risk assessment plus the apparent condition of the drums dictated that they be buried at an approved site or detonated under controlled conditions at a remote site. The latter was chosen. It was also recommended by the manufacturer that the number of times that the trailers were to be moved be kept to an absolute minimum to prevent jarring of the drums and the production of sparks that could initiate an explosion. The move to the remote site was effected without any trouble.

To assess the area around the temporary storage site that would have been affected by a release of phosphine, certain assumptions were necessary. It was assumed that only one drum at a time would corrode through and leak the gas to the atmosphere, and the amount of gas released in one leak would be 136 kg. The assessment was to be performed on the Hazard Assessment Computer System (HACS); however, it was learned that phosphine was not listed in the CHRIS catalog of chemical data so HACS could not

execute the assessment. It was later determined that hydrogen sulphide would be a good substitute, since its molecular weight (34) and vapour density (1.2) are almost identical to those of phosphine. The HACS input parameters (assumptions) were as follows:

1. HACS Model C is the appropriate model for this assessment.
2. The release of gas is instantaneous.
3. The total mass of gas released is 136 kg.
4. The gas is released from a circular-shaped source 10 ft. (3.048 m) in diameter situated at ground level.
5. The air temperature is 50°F (10°C).
6. The wind speed is 5 knots (2.57 m/s).
7. The lower toxicity limit (acute) for the gas is 0.3 ppm.
8. The "critical location" to be used as a reference point for measuring the toxicity level versus time and distance from the site is plotted at 1 mile (1609 m) directly downwind of the discharge site and 6 feet (1.83 m) above ground level; x = 1 mile, y = 0, z = 6 feet (1.83 m).

Based on the above input, the following hazard assessment was obtained:

1. The maximum downwind distance over which the PH_3 concentration will remain above 0.3 ppm will be 2.7 miles (4345 m).
2. The vapour will tend to remain near the ground since the vapor density ratio is greater than 1.
3. At 1 mile downwind, the concentration of PH_3 will reach 0.3 ppm within 8 minutes after release.
4. At 1 mile downwind, the concentration will peak out 10 minutes after the release and then begin to decline.
5. At 1 mile downwind, the PH_3 concentration will fall below 0.3 ppm 13 minutes after release.
6. During the period when the concentration of vapour is toxic at 1 mile downwind (5 minutes), the toxic cloud will extend approximately 0.2 miles (322 m) on both sides of downwind centerline at that point.

Table 6 shows the time that the PH_3 concentration reaches 0.3 ppm at various downwind distances, the duration that the concentration remains above 0.3 ppm and the crosswind distance described in number 6.

10.2.1 Hazard Area for Phosphine. From the above data, it was ascertained that the main phosphine toxicity hazard from the instantaneous release of one drum would be within an area 2.7 miles (4345 m) x 0.4 miles (644 m), centered on a line downwind of the release area. Since the direction of the wind can and does change rapidly, it was assumed that the populace residing within a 2.7 mile (4345 m) radius of the Ryder terminal was threatened by the phosphine.

TABLE 6 PHOSPHINE VAPOUR CLOUD HAZARD DATA

Downwind Distance (m)	Downwind Distance (Feet)	Arrival Time (minutes)	1/2 Hazard Zone (m)	1/2 Hazard Zone (Feet)	Duration (minutes)
10.76	35.3	0.0	28.63	93.92	0.3710
94.88	311.3	0.1681	68.95	226.2	0.8935
179.0	587.3	0.4996	101.9	334.3	1.321
263.1	863.2	0.8557	130.8	429.0	1.695
344.4	1130.0	1.235	156.7	514.2	2.031
431.3	1415.0	1.626	180.4	591.9	2.338
515.4	1691.0	2.030	202.2	663.4	2.621
599.5	1967.0	2.444	222.4	729.6	2.882
683.7	2243.0	2.868	241.2	791.2	3.125
767.8	2519.0	3.300	258.6	848.5	3.352
851.9	2795.0	3.739	274.9	902.0	3.352
936.0	3071.0	4.185	290.1	951.9	3.760
1020.0	3347.0	4.635	304.8	1000.0	3.951
1104.0	3623.0	5.095	318.2	1044.0	4.122
1188.0	3899.0	5.560	330.4	1084.0	4.282
1273.0	4175.0	6.031	341.7	1121.0	4.430
1357.0	4451.0	6.508	352.3	1156.0	4.567
1441.0	4727.0	6.989	362.1	1188.0	4.694
1525.0	5003.0	7.476	371.2	1218.0	4.810
1609.0	5279.0	7.968	379.5	1245.0	4.916

10.2.2 Phosphoric Oxide/Acid Hazard. It was also necessary to assess the area which would be affected by the explosion of a drum and the sequence of events which such an occurrence would trigger. The explosion would result in the rapid oxidation of the phosphorus to form phosphorus pentoxide and its subsequent hydration to form phosphoric acid in micro-particulate form similar in character to a dust. The "Instantaneous Point Source Technique" was used as presented in the USEPA Office of Air Programs Publication No. AP26 (March 1972), Workbook of Atmospheric Dispersion Estimates to produce phosphoric acid plume approximations for stable, neutral, and unstable atmospheric conditions.

10.2.2.1 Stable atmosphere. This condition is characteristic of weather conditions at night when there is an open sky and little wind, or during the day when there is a cloud cover and little wind. The data for this condition are presented in Table 7 below.

TABLE 7 DOWNWIND PHOSPHORUS PENTOXIDE CONCENTRATIONS AT VARIOUS DISTANCES IN STABLE ATMOSPHERE

Downwind Distance from Release	Conc. for 100 lbs. (45.36 kg) (ppm)	Conc. for 10 000 lbs. (4536 kg) (ppm)	Conc. for 20 000 lbs. (9072 kg) (ppm)	Con. for 35 000 lbs. (15 876 kg) (ppm)
100 m	16 571	Very high	Very high	Very high
400 m	391	39 100	78 200	136 850
1 km	39	3 900	7 800	136 500
4 km	1.3	130	260	455
10 km	0.15	15	30	52.5
40 km	0.012	1.2	2.4	4.2

10.2.2.2 Neutral atmosphere. This condition is characteristic of weather conditions when there is a cloudy or overcast sky and moderate winds. The data obtained for this condition are presented in Table 8.

TABLE 8 DOWNWIND PHOSPHORUS PENTOXIDE CONCENTRATIONS AT VARIOUS DISTANCES IN NEUTRAL ATMOSPHERE

Downwind Distance from Release	Conc. for 100 lbs. (45.36 kg) (ppm)	Conc. for 10 000 lbs. (4536 kg) (ppm)	Conc. for 20 000 lbs. (9072 kg) (ppm)	Con. for 35 000 lbs. (15 876 kg) (ppm)
100 m	6 985	698 000	Very high	Very high
500 m	94.6	9 460	18 930	33 110
1 km	13.0	1 300	2 600	4 500
5 km	0.26	260	520	910
10 km	0.05	5	10	17.5
50 km	0.0012	0.12	0.24	0.42

10.2.2.3 Unstable atmosphere. This condition is representative of weather conditions when there are high winds, little if any cloud cover, and a turbulent atmosphere which generally promotes rapid mixing. The data obtained for this condition are presented in Table 9.

TABLE 9 DOWNWIND PHOSPHORUS PENTOXIDE CONCENTRATIONS AT VARIOUS DISTANCES IN UNSTABLE ATMOSPHERE

Downwind Distance from Release	Conc. for 100 lbs. (45.36 kg) (ppm)	Conc. for 10 000 lbs. (4536 kg) (ppm)	Conc. for 20 000 lbs. (9072 kg) (ppm)	Con. for 35 000 lbs. (15 876 kg) (ppm)
100 m	1 643	164 300	328 600	575 050
50 m	40	4 000	8 000	14 000
1 km	3.4	340	680	1 190
4 km	0.07	7	14	24.5
10 km	0.006	0.6	1.2	2.1
40 km	0.00015	0.015	0.03	0.525

10.2.3 Hazard Area for Phosphoric Acid. In assessing the hazard area for phosphorus pentoxide, one had to assume the worst, feasible case, i.e., that the entire contents of one trailer would explode if one drum exploded and that this would occur at a time when the atmosphere was stable. Since one trailer contained 32 drums (12 800 lbs. (5806 kg)) and the other 55 drums (22 000 lbs. (9979 kg)), the hazard area was estimated from Table 7 by using the 10 000 lbs. (4536 kg) and 20 000 lbs. (9072 kg) release columns, respectively. From these data and the TLV (1 ppm), it was determined that an area extending approximately 24 miles (38 624 m) downwind would reach concentrations in excess of this level. Since phosphorus pentoxide is not considered an extremely poisonous material, and since the TLV is the concentration considered to be safe for continuous exposure for 8 hours, an Emergency Exposure Limit (EEL) of 10 ppm was established. At this concentration, a hazard area extending approximately 8-10 miles (12 875-16 093 m) downwind can be estimated. It was this distance that was agreed upon and an evacuation radius of 10 miles (16 093 m) was derived when it was considered that the wind can change direction more rapidly than the populace can be evacuated.

As has been stated on many occasions in this manual, the fume cloud formed by the combustion of white phosphorus is a complicated mixture of oxides and hydrolysis products and precursors. It is felt the preceding assessments for a simplified cloud of only phosphorus pentoxide or phosphoric acid are acceptable, however, since it would be impossible to predict the actual composition and ratio of components comprising the cloud. Also, since the cloud components will extract water from the atmosphere and in so doing gain mass, the phosphoric acid assessment should represent a worst case situation mass-wise.

As can be seen from the overall description of this particular incident, the events encountered in any given incident may lead to far more complicated post events than just those associated with removal/recovery of the spilled chemical (in this case white phosphorus) and the subsequent cleanup of the spill area. The main article from which the above description was extracted concentrated on and emphasized the final method of disposal for the damaged drums of white phosphorus (namely, controlled detonation by a military disposal team at a remote military site). This is always a viable choice if the circumstances dictate it and the remote site is reasonably accessible. The rewrite for this manual, however, was restructured to emphasize the events that took place prior to the actual disposal. The reader may refer to the reference for details of the latter. It is to be pointed out again that the properties and chemistry of phosphorus are complicated and should be reviewed in this manual by all personnel related in any way to the emergency response community. The lessons learned from this incident are straightforward and readily discernible from the above text. They are therefore not repeated in these concluding remarks.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was to assume that samples of various materials and environmental media - air, water, soil - would be analyzed in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought. If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Methods for the Detection of White Phosphorus and Phosphorus Oxides/Phosphoric Acid in Air

Because white phosphorus is spontaneously flammable in air, it is generally assumed that all airborne phosphorus will be in the form of oxides, primarily phosphorus pentoxide, and in particulate form. Furthermore, since the oxides have a great affinity for water, they will combine with atmospheric moisture to form the various oxyacids and intermediates thereof. The literature, however, indicates there is a concentration range above and below which the oxidation reaction between phosphorus vapour and oxygen is very slow (Van Wazer 1958; Rushing 1962; Bullock 1969 IN Jangaard 1972). Other investigators found that white phosphorus, when placed under soil (two types used in experiments), partially escaped from the soil surface as predominantly unreacted phosphorus vapour mixed with oxides for several days after placement (Warnock 1972). Since an accident involving a large quantity of white phosphorus would more than likely involve a fire, it must be assumed that large quantities of combustion products would form the major fume cloud. It is therefore thought appropriate to include detection methods for both white phosphorus (site monitoring after cleanup) and phosphoric acid (fume cloud).

11.1.1 Gas Chromatography for White Phosphorus (Bohl 1973). Under typical test conditions, as little as 10^{-11} g (0.0004 mg P_4/m^3 of air) of elemental phosphorus can be detected. Long-term reproducibility over the range studied was $\pm$ 0.003 mg/m^3.

Samples are collected by drawing 0.42-0.85 m^3 of air at a rate of 4.7 x 10^{-4} m^3/s through two Smith-Greenburg impingers arranged in series. Each impinger contains 100 mL of xylene. A Gelman twin-cylinder vacuum pump and a dry gas meter are used. Evaporation may occur in the first impinger and must be taken into account in the calculations. Sample volumes must be corrected to standard conditions.

To differentiate between gaseous phosphorus and phosphorus-bearing particulates, two samples should be collected at each location studied. One sample should be unfiltered and the other filtered through a Millipore• filter of 0.8 μ pore size. The samples are now ready for analysis.

The gas chromatograph used to develop this method was a Tracor Model MT-220. Conditions for the test are:

Column:	6 ft. x 1/4 in. glass, U-shaped, packed with 3.8% SE-30 silicone gum rubber on 80-100 mesh Chromosorb W
Column Temperature:	80°C
Injector Temperature:	235°C
Detector Temperature:	185°C
Carrier Gas:	Nitrogen (32 psi, rotameter 9.5)
Sample Size:	6 μL

The flame photometric detector consists basically of a fuel-rich hydrogen-air flame, a narrow bandpass interference filter and a photomultiplier tube. Sample components, after separation on a chromatographic column, are swept into the flame. Phosphorus compounds emit light at 526 nm which is measured and related to the concentration of the compound being eluted. The detector responds to all volatile phosphorus compounds. Hydrocarbons and compounds containing halogens, nitrogen and oxygen are essentially undetected.

A series of standard solutions of phosphorus in xylene must be prepared as follows. Rinse a small, clean piece of white phosphorus with acetone and dry in a stream of nitrogen. Weigh by adding to a tared vial of water. Dry again and dissolve in a measured volume of xylene.

From this stock solution, standards in the range 0.046-1.84 mg/L, or any other concentration desired, can be prepared. The solutions can be stored for at least 8 months

in the dark with no apparent change in phosphorus concentration. An inert gas cover is not necessary.

Since the enormous volume of solvent compared to phosphorus may extinguish the flame of the detector, a solvent venting system probably should be incorporated before the solvent reaches the detector.

Phosphine will elute about 10 times faster than white phosphorus under the conditions stated.

11.1.2 Membrane Filter Method for Phosphoric Acid (NIOSH 1977). A range of 0.2-4.0 mg/m^3 of phosphoric acid in a 50 L sample of air can be determined spectrophotometrically by the molybdenum blue method after collection on a membrane filter. Simply stated, particulate matter containing phosphoric acid is collected on a membrane filter. The filter is extracted with water and the dissolved phosphate ion is determined spectrophotometrically.

Air is sampled through a filter for about 1 h at 1.5-2.0 L/min. The sampling time depends on the concentration of phosphoric acid expected. The cellulose ester membrane filter, 0.8 µm pore size, should be 37 mm in diameter and Millipore Type AA, or equivalent. The 37 mm plastic filter holder is a Millipore MAWP 037 AO type, or equivalent. A typical calibrated sampling pump is used for the process.

The filter is removed from the holder and placed in a 125 mL Phillips beaker. Distilled water, 5 mL, warmed to 40-60°C is added to the beaker, swirled, and decanted into a 50 mL volumetric flask. This process is repeated 5 times. Then 5 mL of molybdate solution and 2 mL of hydrogen sulphate solution are added to the flask. The total volume of the flask is increased to 50 mL by the addition of distilled water. This mixture is stirred thoroughly. The volumetric flask is then immersed in a boiling water bath for 10 min followed by rapid cooling. The absorbance is measured at 830 nm in 1 cm cell. A reagent blank is used in the reference cell.

Reagents used for this procedure should be analytical reagent grade; water should be doubly distilled. The standard phosphate solution is prepared by dissolving 0.1389 g of potassium dihydrogen phosphate (KH_2PO_4), in water and diluting to 1 L. This solution contains 100 µg/mL of H_3PO_4. The molybdate solution is prepared by dissolving 25 g of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) in 10 N sulphuric acid and diluting to 1 L with 10 N sulphuric acid. The hydrazine sulphate solution is prepared by dissolving 1.5 g of hydrazine sulphate ($H_3NNH_3SO_4$) in water and diluting to 1 L.

The amount of phosphoric acid (in μg) in the sample is read from a calibration curve previously prepared.

11.2 Qualitative Methods for the Detection of White Phosphorus and Phosphorus Oxides/Phosphoric Acid in Air

11.2.1 White Phosphorus. Air is sampled as described in Section 11.1.1 without a filter. The xylene is washed several times with oxidant-free water in a separatory funnel. This process removes any oxides trapped in the impinger solution. The xylene solution is then shaken with a 1 percent aqueous solution of silver nitrate. The resulting black precipitate of silver phosphide[a] is treated with 5 percent aqueous solution of sodium bromide saturated with bromine. Concentrated nitric acid is added and the solution of oxidation product boiled. This is followed by a few drops of hot 0.1 M ammonium molybdate solution. The solution can be warmed (do not boil). A yellow precipitate of ammonium phospho-molybdate ($(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O$) indicates the presence of phosphate ion (oxidized white phosphorus) (modified from Warnock 1972; Welcher 1955; Hogness 1954).

11.2.2 Phosphate Ion. Several qualitative tests for the presence of the phosphate ion (PO_4^{-3}) were reviewed in a standard qualitative analysis textbook (Hogness 1954). The test chosen for inclusion in this manual involves several initial steps to ensure the test is not interfered with by the presence of the arsenate ion (ASO_4^{-3}), regardless of how unlikely its presence is anticipated.

Air is sampled as described in Section 11.1.1. The filter is treated as described in the same section, except the beaker can be decanted into another beaker and the action repeated as indicated. A 1 mL volume of sample is placed in a 25 mL test tube and then 4 mL of 6 M hydrochloric acid are added. One drop of 1 M ammonium iodide (NH_4I) is added, the solution heated to boiling and saturated with hydrogen sulphide gas. The solution is centrifuged and the supernatant placed in a small casserole and evaporated almost to dryness. The preceding steps are to be carried out in a fume hood. To the residue in the casserole are added 5 drops of 15 M nitric acid (HNO_3) and 5 drops of water. This is followed by 10 drops of hot 0.1 M ammonium molybdate solution. The solution can be warmed (do not boil). A yellow precipitate of ammonium phospho-

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a Probably AgP_3 or AgP_2. Van Wazer (1958) indicates there is an Ag_3P, but it is formed by mixing phosphine (PH_3) with aqueous silver nitrate. Van Wazer also states white phosphorus is oxidized by aqueous solutions of salts of metals, such as Ag, which have a low redox potential.

molybdate ($(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O$) indicates the presence of phosphate ion (Welcher 1955; Hogness 1954).

11.3 Quantitative Method for the Detection of White Phosphorus in Water

White phosphorus is extracted from the water samples by vigorous shaking with either pesticide-quality benzene or isooctane. The aqueous-organic extractant ratio on a volume-to-volume basis is 2:1. The operation should be carried out in an inert atmosphere of nitrogen or argon. Samples with suspected large amounts of white phosphorus should be extracted with fresh solvent one additional time.

Chromatography for the development of this technique was carried out on a MicroTek 220. It was fitted with a Melpar flame photometric detector (FPD) employing a 526 nm filter. Signals were recorded on Honeywell Electronik I-mV recorders fitted with disc integrators. Conditions for chromatography were:

Instrument:	MicroTek
Column:	2 m x 3 mm U-glass
Packing:	OVI, 3% on Chromosorb W
Column Temperature:	100°C
Injector Temperature:	200°C
Detector Temperature:	200°C
Carrier Gas Flow:	He, 80 mL/min

The hydrogen, oxygen and air flows are those specified in the FDP manufacturers' instructions. All injections should be made using Hamilton No. 701 syringes. Under these conditions, phosphorus will be eluted as a sharp peak about 2 min after injection.

Detector response may vary slightly from day to day, possibly because of small variations in flame characteristics. As a result, a calibration curve must be plotted immediately before each series of analyses. Standard solutions should be prepared by weighing a clean piece of white phosphorus under water in a tared vial. It is then dried with acetone (10 s immersion) and dissolved in benzene. The standard solutions should be stored at 0°C in the dark under an argon atmosphere. Solutions are stable for several weeks if used daily, or longer if only used occasionally to prepare fresh dilutions.

At best, the FPD will detect about 10^{-12} g of white phosphorus, but the accuracy may be $\pm$ 100 percent. To increase the sensitivity of the method, concentrations

of the organic extracts may be warranted. This can be accomplished by carefully evaporating the solvent under a gentle stream of inert gas, never going to dryness.

11.4 Qualitative Method for the Detection of White Phosphorus in Water

Use process described in Section 11.2.1.

11.5 Quantitative Method for the Detection of White Phosphorus in Soil

Extract the white phosphorus from the soil or sediment with an organic solvent, such as xylene, benzene or isooctane, in an inert atmosphere. The solvent is then filtered free of solid. The extraction process should be carried out several times with relatively small portions of solvent. The detection method can be that described in Sections 11.1.1 or 11.3.1.

11.6 Qualitative Method for the Detection of White Phosphorus in Soil

After the white phosphorus is extracted from the soil as described in Section 11.5, the method described in Section 11.2.1 can be used.

12 REFERENCES AND BIBLIOGRAPHY

12.1 References

AAR 1981: BDM Corporation, The AAR Hazardous Materials Data Base, Prepared for the Association of American Railroads, Parts I and II, McLean, VA. (May, 1981).

AOAC 1925: Association of Official Agricultural Chemists, Methods of Analysis, AOAC, Washington, DC., p. 31. (1925).

ASTM 1979: American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31, Water, Philadelphia, PA, D1192, D3370, D515, (Method C). (1979).

Bailar 1973: Bailar J.C., et al. (ed.), Comprehensive Inorganic Chemistry, Pergamon Press, Oxford. (1973).

Bentley 1978: Bentley, R.E., Buxton, K.S., Sleight, B.H., Acute Toxicity of Five Munitions Compounds to Aquatic Organisms, Interim Report to U.S. Army Medical Research and Development Command, Washington, DC, No. DAMO-17-74-R-4755. (1978).

Bohl 1973: Bohl, C.D., Kaelble, E.F., "Determination of Elemental Phosphorus in Air by Gas Chromatography", American Industrial Hygiene Association Journal, Vol. 34, No. 7, pp. 306-309. (July, 1973).

Bretherick 1979: Bretherick, L., Handbook of Reactive Chemical Hazards, Second Edition, Butterworths, London, England. (1979).

Brutsaert 1981: Brutsaert, W.F., Hedstrom, W.E., McNeice, T.G., "Effect of Soil Moisture Content Upon Adsorption and Movement of Phosphorus from Leachates of Domestic Waste Disposal Systems", Gov't. Reports Announcements and Index, (GRA & I), No. 21. (1981).

Campbell 1977: Campbell, D.L., Oxidation of Phossy Water by Ozone, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, AD 044753. (September, 1977).

CBG 1980: Southam Business Publications Ltd., "1981 Chemical Buyers' Guide", Canadian Chemical Processing, Vol. 64, No. 9, Don Mills, Ontario. (December, 1980).

CCP 1981: "Plant Revamp for Phosphorus", Canadian Chemical Processing, Vol. 65, No. 7, p. 14. (October 30, 1981).

CDS 1967: National Association of Corrosion Engineers, Corrosion Data Survey, Houston, TX. (1967).

CG-D-56-78: Hand, T.D., et al., A Feasibility Study of Response Techniques for Discharges of Hazardous Chemicals that Sink, U.S. Coast Guard, Washington, DC, CG-D-56-78. (June, 1978).

CHRIS 1978: U.S. Department of Transportation, Coast Guard, Chemical Hazards Response Information System (CHRIS), Washington, DC. (1978).

CMI 1980: Barry, G.S., "Phosphate", Canadian Mineral Industry. (1980).

Corpus 1982: Corpus Information Services Ltd., "Phosphorus", Chemical Product Profiles, Don Mills, Ontario, revised. (October, 1982).

Cote 1971: Cote, R.P., Laboratory Studies on the Effects of Elemental Phosphorus on Selected Marine Organisms, M.Sc. Thesis, Department of Biology, Memorial University of Newfoundland, St. John's, Newfoundland. (1971).

Cotton 1972: Cotton, F.A., Wilkinson, G., Advanced Inorganic Chemistry, Interscience Publishers, New York, NY. (1972).

CRC 1957: Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland, OH. (1957).

CRC 1980: Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 60th Edition, Chemical Rubber Publishing Company, Cleveland, OH. (1980).

CRC 1982: Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 62nd Edition, Chemical Rubber Publishing Company, Cleveland, OH. (1982).

CRC 1983: Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 63rd Edition, Chemical Rubber Publishing Company, Cleveland, OH. (1983).

CTC 1974: Canadian Transport Commission, Regulations for the Transportation of Dangerous Commodities by Rail, Department of Supply & Services, Ottawa. (July 31, 1974).

DCRG 1978: Dow Chemical Company, Dow Chemical Resistance Guide for Dow Plastic Lined Piping Products, Midland, MI. (1978).

Doc. TLV 1981: American Conference of Governmental Industrial Hygienists (ACGIH), Documentation of Threshold Limit Values, Fourth Edition, Cincinnati, OH. (1981).

DPPED 1967: DOM-X, DOM-X Plastic Pipe Engineering Data, Toronto, Ontario. (1967).

Ducre 1974: Ducre, J.C., Rosenblatt, D.H., Mammalian Toxicology and Toxicity to Aquatic Organisms of Four Important Types of Waterborne Munitions Pollutants, NTIS AD-778-725. (March, 1974).

EPA 600/2-80-076: Hatayama, H.K., Chen, J.J., deVera, E.R., Stephens, R.D., Storm, D.L., A Method for Determining the Compatibility of Hazardous Wastes, Municipal Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH. (April, 1980).

EPA 600/8-80-042E: Environmental Protection Agency, Treatability Manual, Volume V, Summary, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, EPA 600/8-80-042E. (July, 1980).

EPA 670/2-75-042: Pilie, R.J., et al., Methods to Treat, Control and Monitor Spilled Hazardous Materials, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, OH, EPA 670/2-75-042. (June, 1975).

Erco ERF: Erco Industries Ltd. Emergency Response Forum on Yellow Phosphorus in Water, Islington, Ontario. Not dated.

Erco PDS: Erco Industries Ltd., Product Data Sheet, Islington, Ontario. Not dated.

Erco 1983: Erco Industries Ltd., Properties and Essential Information for the Safe Handling of Phosphorus (White or Yellow), Islington, Ontario. (30 June 1983).

Erco 1983a: Personal Communication, Erco Industries Ltd., Islington, Ontario. (December, 1983).

ERG 1980: U.S. Department of Transportation, Hazardous Materials, 1980 Emergency Response Guidebook, U.S. Department of Transportation, Research and Special Programs Administration, Materials Transportation Bureau, Washington, DC. (1980).

FKC 1975: Lowenheim, F.A., Moran, M.K., Faith, Keye's and Clark's Industrial Chemicals, Wiley-Interscience, New York, NY. (1975).

Fletcher 1971: Fletcher, G.L., Hoyle, R.J., Horne, D.A., "The Relative Toxicities of Yellow Phosphorus Production Wastes to Seawater-Maintained Fish", Fisheries Research Board Canada Tech. Bull., No. 255. (1971).

GE 1977: General Electric Company, Material Safety Data Sheets, Material Safety Information Services, Schenectady, NY. (September/October, 1977).

Gillelan 1983: Gillelan, D., Corporate Traffic Manager, Erco Industries Ltd., Personal Communication, Telcon. (December 14, 1983).

Goodman 1980: Goodman, L.S., et al. (ed.), The Pharmacological Basis of Therapeutic, Sixth Edition, MacMillan Publishing Co. Inc., New York, NY. (1980).

Gosselin 1976: Gosselin, R.E., et al., Chemical Toxicology of Commercial Products, The Williams & Wilkinson Co., Baltimore, MD. (1976).

Hawley 1977: Hawley, G.G., The Condensed Chemical Dictionary, 9th Edition, Van Nostrand Reinhold Co., New York, NY. (1977).

Hill 1981: Hill, D.E., Sawhney, B.L., "Removal of Phosphorus from Waste Water by Soil Under Aerobic and Anaerobic Conditions", J. Environ. Qual., Vol. 10, No. 3, pp. 401-405. (1981).

HMN 1980: Hazardous Materials Newsletter, "White Phosphorus Fire", Barre, VT, p. 9. (1 October 1980).

Hogness 1954: Hogness, T.R., Johnson, W.C., Qualitative Analysis and Chemical Equilibrium, 4th Edition, Holt, Rinebart and Winston, Inc., New York. (1954).

Hooker DS 1979: Hooker Chemicals and Plastics Corporation, Data Sheet No. 732, Electrochemical Division, Taft, LA. (December, 1979).

Hooker DS 1980: Hooker Chemicals and Plastics Corporation, Hooker Chemical Data Sheet No. 796-B, "Amorphous Phosphorus Red", Process Chemical Division, Niagara Falls, NY. (April, 1980).

Hooker MSDS 1980: Hooker Chemicals and Plastics Corporation, Material Safety Data Sheet, "Red Phosphorus", Niagara Falls, NY. (April, 1980).

ITII 1981: International Technical Information Institute, Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data, Japan. (1981).

JANAF 1971: Stull, D.R., Prophet, H., JANAF Thermochemical Tables, Second Edition, Office of Standard Reference Data, U.S. National Bureau of Standards, Washington, DC. (June, 1971).

Jangaard 1972: Jangaard, P.M., Effects of Elemental Phosphorus on Marine Life, Fisheries Research Board of Canada, Circular No. 2, Halifax, N.S. (November, 1972).

Jorgensen 1979: Jorgensen, S.E. (ed.), Handbook of Environmental Data and Ecological Parameters, International Society for Ecological Modelling, Pergamon Press, Oxford, England, p. 470. (1979).

Kirk-Othmer 1981: Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, John Wiley & Sons, New York. (1981).

Kirk-Othmer 1982: Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 19, John Wiley & Sons, New York, NY. (1982).

Kurita 1981: Kurita Water Industries Ltd., "Phosphorus Removal From Waste Waters", Jpn. Kokai Tokkyo Koho, Patent No. 81-65693. (March, 1981).

Lafornara 1980: Lafornara, J.P., Massey, I.T., The Disposal of Fire Damaged White Phosphorus Drums, Proceedings of the 1980 National Conference on Control of Hazardous Material Spills, Louisville, KY. (May 13-15, 1980).

Lakhnova 1975: Lakhnova, Va., Sarat, T.R., "Effects of Elemental Phosphorus on *Daphnia Magna* (straus)", OTD Gosniovkh., Vol. 13, pp. 206-207. (1975).

Lyon 1980: Lyon, H.W., Woo, C.S., "Accelerated Uptake Response of Green Alga, *Chlorella vulgaris*, to High Levels of Phosphorus in Mississippi River Water", Sci. Total Environ., Vol. 14, No. 3, pp. 279-285. (1980).

MCA 1947: Manufacturing Chemists Association, Chemical Safety Data Sheet, "Elemental Phosphorus", Washington, DC. (1947).

MCA 1976: Manufacturing Chemists Association, "Phosphorus, Elemental", Washington, DC. (1976).

Merck 1976: Windholz, M., Budavari, S., Stroumtsos, L.Y., Fertig, M.N. (ed.), The Merck Index, Ninth Edition, Merck & Co. Inc., Rahway, NJ. (1976).

Merck 1983: Windholz, M., Budavari, S., Blumetti, R.F., Otterbein, E.S. (ed.), The Merck Index, 10th Edition, Merck & Co., Inc., Rahway, NJ. (1983).

Meyer 1977: Meyer, E., Chemistry of Hazardous Materials, Prentice-Hall Inc., Englewood Cliffs, NJ. (1977).

Mobil MSDB 1979: Mobil Chemical Company, Material Safety Data Bulletin, "Elemental Phosphorus", Richmond, VA. (February 27, 1979).

MWPP 1978: Rehau, Mechan-O-Joint Water Pressure Pipe and Fittings, Montreal, Quebec. (1978).

NFPA 1978: National Fire Protection Association, Fire Protection Guide on Hazardous Materials, Seventh Edition, Boston, MA. (1978).

NIOSH 1977: National Institute for Occupational Safety and Health, Manual of Analytical Methods, Second Edition, Vol. 1, Part 1, Cincinnati, OH, P&CAM 216. (April, 1977).

NIOSH 1978: National Institute for Occupational Safety and Health, Manual of Analytical Methods, Second Edition, Vol. 4, Cincinnati, OH, Method No. 5334. (August, 1978).

NIOSH/OSHA 1981: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health (NIOSH), U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), Occupational Health Guidelines for Chemical Hazards, NIOSH Publication No. 81-123. (1981).

NRCC 1981: National Research Council of Canada, Effects of Yellow Phosphorus in the Canadian Environment, NRCC No. 17587, Ottawa, Canada. (1981).

OHM-TADS 1981: Oil and Hazardous Materials Technical Assistance Data System, U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Office of Water Program Operations, Washington, DC. (1981).

O.I. 1970: Oceanology International. (October, 1970).

Partington 1958: Partington, J.R., General and Inorganic Chemistry, Third Edition, MacMillan and Co., London. (1958).

Patty 1981: Clayton, G.D., Clayton, F.E. (ed.), Patty's Industrial Hygiene and Toxicology, Vols. 2A, 2B, Third Revised Edition, John Wiley and Sons Canada Limited, Toronto, Ontario. (1981).

PB 244046: Koyser, E.G., et al., Spontaneously Combustible Solids - A Literature Survey, Report Number TES-20-75-1, Naval Surface Weapons Center, White Oak, Silver Springs. MD. (May, 1975).

Pearson 1978: Pearson, J.G., Robinson, P.E., Bender, E.S., The Toxicity of Phossy Water to Selected Fresh Water Organisms, U.S. NTIS No. AS-A054374. (1978).

Percy 1983: Percy, R., Marine Environment Branch, EPS, Atlantic Region, Private Communication, File No. 4482-9. (March 3, 1983).

Perry 1973: Perry, R.H., Chilton, C.H. (ed.), Chemical Engineer's Handbook, Fifth Edition, McGraw-Hill Book Company, New York, NY. (1973).

Personal Communication with CDF 1982: Personal Communication, California Department of Forestry (CDF), Paris, CA. (June, 1982).

Rav 1975: Rav, H., "Thermodynamics of Dense Phosphorus Vapours", J. Chem. Thermodynamics, Vol. 1, pp. 903-912. (1975).

Riegels 1974: Kent, J.A., Riegels Handbook of Industrial Chemistry, Seventh Edition, Van Nostrand Reinhold Company, New York, NY. (1974).

RTECS 1979: Lewis, R.J., Tatken, R.L., Registry of Toxic Effects of Chemical Substances, 1979, Vols. 1 and 2, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH. (September, 1980).

Rushing 1962: Rushing, D.E., "A Tentative Method for the Determination of Elemental Phosphorus in Air", American Industrial Hygiene Assoc. J., Vol. 23, pp. 383-387. (September-October, 1962).

Sax 1968: Sax, N.I., Dangerous Properties of Industrial Materials Report, Third Edition, Van Nostrand Reinhold Company, New York, NY. (1968).

Sax 1979: Sax, N.I., Dangerous Properties of Industrial Materials, Fifth Edition, Van Nostrand Reinhold Company, New York, NY. (1979).

Stauffer MSDS 1980: Stauffer Chemical Company, Material Safety Data Sheet, Westport, CT. (1980).

Stauffer PSI: Stauffer Chemical Company, Product Safety Information, "Yellow Phosphorus", Westport, CT. Not dated.

Stephenson 1969: Stephenson, C.C., Potter, R.L., Maple, T.G., Morrow, J.C., J, Abein Thermodynamics, Vol. 7, pp. 59-76. (1969).

Steubing 1980: Steubing, E.W., Fricksel, R.H., Reubel, G.O., Recent Research on Phosphorus Smoke, Army Armourment and Development Command, Aberdeen Proving Ground, MD, ADA 090442. (June, 1980).

Streeter 1971: Streeter, V.L., Fluid Mechanics, Fifth Edition, McGraw-Hill Book Company, New York, NY. (1971).

Sullivan 1979: Sullivan, J.H. Jr., Putnam, H.D., Keirn, M.A., Pruitt, B.C. Jr., Nichols, J.C., McClave, J.T., "A Summary and Evaluation of Aquatic Environmental Data in Relation to Establishing Water Quality Criteria for Munitions-Unique Compounds. Part 3. White Phosphorus", Final Report, Water and Air Research, Inc., Gainesville, FL. (April, 1979).

TCM 1979: General American Transportation Corporation, Tank Car Manual, Chicago, IL. (May, 1979).

TDB (on-line) 1981: Toxicity Data Base, Toxicology Information On-Line, Available from National Library of Medicine, Washington, DC. (1981).

TDGC 1980: Transport Canada, Transportation of Dangerous Goods Code, Vol. 1 (Lists), Vol. 2, Ottawa, Canada. (June, 1980).

Thibodeaux 1979: Thibodeaux, L.J., Chemodynamics - Environmental Movement of Chemicals in Air, Water and Soil, John Wiley & Sons Inc., New York, NY. (1979).

TLV 1983: American Conference of Governmental Industrial Hygienists, TLV®s Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1983/84, Cincinnati, OH. (1983).

Ullmann 1979: Ullmanns Encyklopaedie der technischen Chemie, Verlag Chemie, Weinheim. (1979).

USDHEW 1977: U.S. Department of Health, Education and Welfare, Occupational Diseases. A Guide to Their Recognition, National Institute for Occupational Safety and Health, DHEW (NIOSH) No. 77-181. (1977).

Van Wazer 1958: Van Wazer, J.R., Phosphorus and its Compounds, Vol. I, Interscience Publishers, Inc., New York. (1958).

Verschueren 1977: Verschueren, K., Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, New York, NY. (1977).

Warwick 1972: Warwick, R.E., "Escape of Elemental Phosphorus from Soil when Applied as White Phosphorus or the Phosphorus-Sulphur Eutectic Solution", J. Environmental Quality, Vol. 1, pp. 311-314. (July-September, 1972).

Wasti 1978: Wasti, K., Abaidoo, K.J.R., Villaume, J.E., A Literature Review - Problem Definition Studies on Selected Toxic Chemicals. Occupational Health and Safety Aspects of Phosphorus Smoke Compounds, Vol. 2, U.S. Army Medical R & D Command, Frederick, MD, AD A056019. (April, 1978).

Water Management Goals 1978: Ontario Ministry of the Environment, Water Management Goals, Policies, Objectives and Implementation Procedures for the Ministry of the Environment, Toronto, Ontario, p. 34. (November, 1978).

Welcher 1955: Welcher, F.J., Hahn, R.B., Semimicro Qualitative Analysis, D. Van Nostrand Co., Inc., Princeton, NJ, p. 458. (1955).

Wicks 1963: Wicks, C.E., et al., Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides and Nitrides, PB 196654, Bureau of Mines, Washington, DC. (1963).

WQC 1972: National Academy of Sciences, Water Quality Criteria 1972; A Report of the Committee on Water Quality Criteria, Environmental Studies Board, National Academy of Sciences, Washington, DC, pp. 253-254. (1972).

WQCDB-2 1971: Environmental Protection Agency, Water Quality Criteria Data Book: Inorganic Chemical Pollution of Freshwater, U.S. Environmental Protection Agency, Water Quality Office, Washington, DC, Vol. 2, p. 239. (1971).

WQCDB-3 1971: Environmental Protection Agency, Water Quality Criteria Data Book: Effects of Chemicals on Aquatic Life, U.S. Environmental Protection Agency, Water Quality Office, Washington, DC, Vol. 3, p. 315. (May, 1971).

WQCDB-5 1973: Environmental Protection Agency, Water Quality Criteria Data Book: Effects of Chemicals on Aquatic Life, U.S. Environmental Protection Agency, Water Quality Office, Washington, DC, Vol. 5. (September, 1973).

WQS 1979: McNeily, R.N., Neimans, V.P., Dwyer, L., Water Quality Sourcebook: A Guide to Water Quality Parameters, Inland Waters Directorate, Water Quality Branch, Environment Canada, Ottawa, Canada, pp. 46, 77, 86. (1979).

Zitko 1970: Zitko, V., Aiken, D.E., Tibbo, S.W., et al., "Toxicity of Yellow Phosphorus to Herring (*Clupea Harengus*), Atlantic Salmon (*Salmo Salar*), Lobster (*Homarus Americanus*) and Beach Flea (*Gammarus Oceanicus*)", Journal of Fisheries Research Board of Canada, Vol. 27, pp. 21-29. (1970).

12.2 Bibliography

American Conference of Governmental Industrial Hygienists (ACGIH), Documentation of Threshold Limit Values, Fourth Edition, Cincinnati, OH. (1981).

American Conference of Governmental Industrial Hygienists, TLV®s Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1983/84, Cincinnati, OH. (1983).

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31, Water, Philadelphia, PA, D1192, D3370, D515, (Method C). (1979).

Association of Official Agricultural Chemists, Methods of Analysis, AOAC, Washington, DC., p. 31. (1925).

Bailar, J.C., et al. (ed.), Comprehensive Inorganic Chemistry, Pergamon Press, Oxford. (1973).

Barry, G.S., "Phosphate", Canadian Mineral Industry. (1980).

BDM Corporation, The AAR Hazardous Materials Data Base, Prepared for the Association of American Railroads, Parts I and II, McLean, VA. (May, 1981).

Bentley, R.E., Buxton, K.S., Sleight, B.H., Acute Toxicity of Five Munitions Compounds to Aquatic Organisms, Interim Report to U.S. Army Medical Research and Development Command, Washington, DC., No. DAMO-17-74-R-4755. (1975).

Bohl, C.D., Kaelble, E.F., "Determination of Elemental Phosphorus in Air by Gas Chromatography", American Industrial Hygiene Association Journal, Vol. 34, No. 7, pp. 306-309. (July, 1973).

Bretherick, L., Handbook of Reactive Chemical Hazards, Second Edition, Butterworths, London, England. (1979).

Brutsaert, W.F., Hedstrom, W.E., McNeice, T.G., "Effect of Soil Moisture Content Upon Adsorption and Movement of Phosphorus from Leachates of Domestic Waste Disposal Systems", Gov't. Reports Announcements and Index, (GRA & I), No. 21. (1981).

California Department of Forestry (CDF), Paris, CA, Personal Communication. (June, 1982).

Campbell, D.L., Oxidation of Phossy Water by Ozone, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, AD 044753. (September, 1977).

Canadian Transport Commission, Regulations for the Transportation of Dangerous Commodities by Rail, Dept. of Supply & Services, Ottawa. (July 31, 1974).

Clayton, G.D., Clayton, F.E. (ed.), Patty's Industrial Hygiene and Toxicology, Vols. 2A, 2B, Third Revised Edition, John Wiley and Sons Canada Limited, Toronto, Ontario. (1981).

Corpus Information Services Ltd., "Phosphorus", Chemical Product Profiles, Don Mills, Ontario, revised. (October, 1982).

Cote, R.P., Laboratory Studies on the Effects of Elemental Phosphorus on Selected Marine Organisms, M.Sc. Thesis, Department of Biology, Memorial University of Newfoundland, St. John's, Newfoundland. (1971).

Cotton, F.A., Wilkinson, G., Advanced Inorganic Chemistry, Interscience Publishers, New York, NY. (1972).

DOM-X, DOM-X Plastic Pipe Engineering Data, Toronto, Ontario. (1967).

Dow Chemical Company, Dow Chemical Resistance Guide for Dow Plastic Lined Piping Products, Midland, MI. (1978).

Ducre, J.C., Rosenblatt, D.H., Mammalian Toxicology and Toxicity to Aquatic Organisms of Four Important Types of Waterborne Munitions Pollutants, NTIS AD-778-725. (March, 1974).

Environmental Protection Agency, Treatability Manual, Volume V, Summary, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, EPA 600/8-80-042E. (July, 1980).

Environmental Protection Agency, Water Quality Criteria Data Book: Inorganic Chemical Pollution of Freshwater, U.S. Environmental Protection Agency, Water Quality Office, Washington, DC, Vol. 2, p. 239. (1971).

Environmental Protection Agency, Water Quality Criteria Data Book: Effects of Chemicals on Aquatic Life, U.S. Environmental Protection Agency, Water Quality Office, Washington, DC, Vol. 3, p. 315. (May, 1971).

Environmental Protection Agency, Water Quality Criteria Data Book: Effects of Chemicals on Aquatic Life, U.S. Environmental Protection Agency, Water Quality Office, Washington, DC, Vol. 5. (September, 1973).

Erco Industries Ltd., Emergency Response Forum on Yellow Phosphorus in Water, Islington, Ontario. Not dated.

Erco Industries Ltd., Product Data Sheet, Islington, Ontario. Not dated.

Erco Industries Ltd., Properties and Essential Information for the Safe Handling of Phosphorus (White or Yellow), Islington, Ontario. (June 30, 1983).

Fletcher, G.L., Hoyle, R.J., Horne, D.A., "The Relative Toxicities of Yellow Phosphorus Production Wastes to Seawater-Maintained Fish", Fisheries Research Board Canada Tech. Bull., No. 255. (1971).

General American Transportation Corporation, Tank Car Manual, Chicago, IL. (May, 1979).

General Electric Company, Material Safety Data Sheets, Material Safety Information Services, Schenectady, NY. (September/October, 1977).

Gillelan, D., Corporate Traffic Manager, Erco Industries Ltd., Personal Communication, Telcon. (December 14, 1983).

Goodman, L.S., et al. (ed.), The Pharmacological Basis of Therapeutic, Sixth Edition, MacMillan Publishing Co. Inc., New York, NY. (1980).

Gosselin, R.E., et al., Clinical Toxicology of Commercial Products, The Williams & Wilkinson Co., Baltimore, MD. (1976).

Hand, T.D., et al., A Feasibility Study of Response Techniques of Discharges of Hazardous Chemicals that Sink, U.S. Coast Guard, Washington, DC, CG-D-56-78. (June, 1978).

Hatayama, H.K., Chen, J.J., deVera, E.R., Stephens, R.D., Storm, D.L., A Method for Determining the Compatibility of Hazardous Wastes, Municipal Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH. (April, 1980).

Hawley, G.G., The Condensed Chemical Dictionary, 9th Edition, Van Nostrand Reinhold Co., New York, NY. (1977).

Hazardous Materials Newsletter, "White Phosphorus Fire", Barre, VT, p. 9. (1 October 1980).

Hill, D.E., Sawhney, B.L., "Removal of Phosphorus from Waste Water by Soil Under Aerobic and Anaerobic Conditions", J. Environ. Qual., Vol. 10, No. 3, pp. 401-405. (1981).

Hogness, T.R., Johnson, W.C., Qualitative Analysis and Chemical Equilibrium, 4th Edition, Holt, Rinebart and Winston, Inc., New York. (1954).

Hooker Chemicals and Plastics Corporation, Hooker Chemical Data Sheet No. 796-B, "Amorphous Phosphorus Red", Process Chemical Division, Niagara Falls, NY. (April, 1980).

Hooker Chemicals and Plastics Corporation, Material Safety Data Sheet, "Red Phosphorus", Niagara Falls, NY. (April, 1980).

Hooker Chemicals and Plastics Corporation, Data Sheet No. 732, Electrochemical Division, Taft, LA. (December, 1979).

International Technical Information Institute, Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data, Japan. (1981).

Jangaard, P.M., Effects of Elemental Phosphorus on Marine Life, Fisheries Research Board of Canada, Circular No. 2, Halifax, N.S. (November, 1972).

Jorgensen, S.E. (ed.)., Handbook of Environmental Data and Ecological Parameters, International Society for Ecological Modelling, Pergamon Press, Oxford, England, p. 470. (1979).

Kent, J.A., Riegels Handbook of Industrial Chemistry, Seventh Edition, Van Nostrand Reinhold Company, New York, NY. (1974).

Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, John Wiley & Sons, New York. (1981).

Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 19, John Wiley & Sons, New York, NY. (1982).

Koyser, E.G., et al., Spontaneously Combustible Solids - A Literature Survey, Report Number TES-20-75-1, Naval Service Weapons Center, White Oaks, Silver Springs, MD. (May, 1975).

Kurita Water Industries Ltd., "Phosphorus Removal From Waste Waters", Jpn. Kokai Tokkyo Koho, Patent No. 81-65693. (March, 1981).

Lafornara, J.P., Massey, I.T., The Disposal of Fire Damaged White Phosphorus Drums, Proceedings of the 1980 National Conference on Control of Hazardous Material Spills, Louisville, KY. (May 13-15, 1980).

Lakhnova, Va., Sarat, T.R., "Effects of Elemental Phosphorus on *Daphnia Magna* (straus)", OTD Gosniovkh., Vol. 13, pp. 206-207. (1975).

Lewis, R.J., Tatken, R.L., Registry of Toxic Effects of Chemical Substances, 1979, Vols. 1 and 2, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH. (September, 1980).

Lowenheim, F.A., Moran, M.K., Faith, Keye's and Clark's Industrial Chemicals, Wiley-Interscience, New York, NY. (1975).

Lyon, H.W., Woo, C.S., "Accelerated Uptake Response of Green Alga, *Chlorella Vulgaris*, to High Levels of Phosphorus in Mississippi River Water", Sci. Total Environ., Vol. 14, No. 3, pp. 279-285. (1980).

Manufacturing Chemists Association, "Phosphorus, Elemental", Washington, DC. (1976).

Manufacturing Chemists Association, Chemical Safety Data Sheet, "Elemental Phosphorus", Washington, DC. (1947).

McNeily, R.N., Neimans, V.P., Dwyer, L., Water Quality Sourcebook: A Guide to Water Quality Parameters, Inland Waters Directorate, Water Quality Branch, Environment Canada, Ottawa, Canada, pp. 46, 77, 86. (1979).

Meyer, E., Chemistry of Hazardous Materials, Prentice-Hall Inc., Englewood Cliffs, NJ. (1977).

Mobil Chemical Company, Material Safety Data Bulletin, "Elemental Phosphorus", Richmond, VA. (February 27, 1979).

National Academy of Sciences, Water Quality Criteria 1972, A Report of the Committee on Water Quality Criteria, Environmental Studies Board, National Academy of Sciences, Washington, DC, pp. 253-254. (1972).

National Association of Corrosion Engineers, Corrosion Data Survey, Houston, TX. (1967).

National Fire Protection Association, Fire Protection Guide on Hazardous Materials, Seventh Edition, Boston, MA. (1978).

National Institute for Occupational Safety and Health, Manual of Analytical Methods, Second Edition, Vol. 4, Cincinnati, OH, Method No. 5334 (August, 1978).

National Institute for Occupational Safety and Health, Manual of Analytical Methods, Second Edition, Vol.1, Part 1, Cincinnati, OH, P&CAM 216. (April, 1977).

National Research Council of Canada, Effects of Yellow Phosphorus in the Canadian Environment, NRCC No. 17587, Ottawa, Canada. (1981).

Oceanology International. (October, 1970).

Oil and Hazardous Materials Technical Assistance Data System, U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Office of Water Program Operations, Washington, DC. (1981).

Ontario Ministry of the Environment, Water Management Goals, Policies, Objectives and Implementation Procedures for the Ministry of the Environment, Toronto, Ontario, p. 34. (November, 1978).

Partington, J.R., General and Inorganic Chemistry, Third Edition, MacMillan and Co., London. (1958).

Pearson, J.G., Robinson, P.E., Bender, E.S., The Toxicity of Phossy Water to Selected Fresh Water Organisms, U.S. NTIS No. AS-A054374. (1978).

Percy, R., Marine Environment Branch, EPS, Atlantic Region, Personal Communication, File No. 4482-9. (March 3, 1983).

Perry, R.H., Chilton, C.H. (ed.), Chemical Engineer's Handbook, Fifth Edition, McGraw-Hill Book Company, New York, NY. (1973).

Personal Communication, Erco Industries Ltd., Islington, Ontario. (December, 1983).

Pilie, R.J., et al., Methods to Treat, Control and Monitor Spilled Hazardous Materials, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, OH, EPA 670/2-75-042. (June, 1975).

"Plant Revamp for Phosphorus", Canadian Chemical Processing, Vol. 65, No. 7, p. 14. (October 30, 1981).

Rav, H., "Thermodynamics of Dense Phosphorus Vapours", J. Chem. Thermodynamics, Vol. 1, pp. 903-912. (1975).

Rehau, Mechan-O-Joint Water Pressure Pipe and Fittings, Montreal, Quebec. (1978).

Rushing, D.E., "A Tentative Method for the Determination of Elemental Phosphorus in Air", American Industrial Hygiene Assoc. J., Vol. 23, pp. 383-387. (September-October, 1962).

Sax, N.I., Dangerous Properties of Industrial Materials Report, Third Edition, Van Nostrand Reinhold Company, New York, NY. (1968).

Sax, N.I., Dangerous Properties of Industrial Materials, Fifth Edition, Van Nostrand Reinhold Company, New York, NY. (1979).

Southam Business Publications Ltd., "1981 Chemical Buyers' Guide", Canadian Chemical Processing, Vol. 64, No. 9, Don Mills, Ontario. (December, 1980).

Stauffer Chemical Company, Product Safety Information, "Yellow Phosphorus", Westport, CT. Not dated.

Stauffer Chemical Company, Material Safety Data Sheet, Westport, CT. (1980).

Stephenson, C.C., Potter, R.L., Maple, T.G., Morrow, J.C., J. Abien, Thermodynamics, Vol. 7, pp. 59-76. (1969).

Steubing, E.W., Fricksel, R.H., Reubel, G.O., Recent Research on Phosphorus Smoke, Army Armourment Research and Development Command, Aberdeen Proving Ground, MD, ADA 090442. (June, 1980).

Streeter, V.L., Fluid Mechanics, Fifth Edition, McGraw-Hill Book Company, New York, NY. (1971).

Stull, D.R., Prophet, H., JANAF Thermochemical Tables, Second Edition, Office of Standard Reference Data, U.S. National Bureau of Standards, Washington, DC. (June, 1971).

Sullivan, J.H. Jr., Putnam, H.D., Keirn, M.A., Pruitt, B.C. Jr., Nichols, J.C., McClave, J.T., "A Summary and Evaluation of Aquatic Environmental Data in Relation to Establishing Water Quality Criteria for Munitions-Unique Compounds. Part 3. White Phosphorus", Final Report, Water and Air Research Inc., Gainesville, FL. (April, 1979).

Thibodeaux, L.J., Chemodynamics - Environmental Movement of Chemicals in Air, Water and Soil, John Wiley & Sons Inc., New York, NY. (1979).

Toxicity Data Base, Toxicology Information On-Line, Available from National Library of Medicine, Washington, DC. (1981).

Transport Canada, Transportation of Dangerous Goods Code, Vol. 1 (Lists), Vol. 2, Ottawa, Canada. (June, 1980).

Ullmanns Encyklopaedie der technischen Chemie, Verlag Chemie, Weinheim. (1975).

U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health (NIOSH), U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), Occupational Health Guidelines for Chemical Hazards, NIOSH Publication No. 81-123. (1981).

U.S. Department of Health, Education and Welfare, Occupational Diseases. A Guide to Their Recognition, National Institute for Occupational Safety and Health, DHEW (NIOSH) No. 77-181. (1977).

U.S. Department of Transportation, Hazardous Materials, 1980 Emergency Response Guidebook, U.S. Department of Transportation, Research and Special Programs Administration, Materials Transportation Bureau, Washington, DC. (1980).

U.S. Department of Transportation, Coast Guard, Chemical Hazards Response Information System (CHRIS), Washington, DC, (1978).

Van Wazer, J.R., Phosphorus and its Compounds, Vol. I, Interscience Publishers Inc., New York. (1958).

Verschueren, K., Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, New York, NY. (1977).

Warwick, R.E., "Escape of Elemental Phosphorus from Soil When Applied as White Phosphorus or the Phosphorus-Sulphur Eutectic Solution", J. Environmental Quality, Vol. 1, pp. 311-314. (July-September, 1972).

Wasti, K., Abaidoo, K.J.R., Villaume, J.E., A Literature Review - Problem Definition Studies on Selected Toxic Chemicals. Occupational Health and Safety Aspects of Phosphorus Smoke Compounds, Vol. 2, U.S. Army Medical R & D Command, Frederick, MD, AD A056019. (April, 1978).

Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 60th Edition, Chemical Rubber Publishing Company, Cleveland, OH. (1980).

Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland, OH. (1957).

Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 62nd Edition, Chemical Rubber Publishing Company, Cleveland, OH. (1982).

Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 63rd Edition, Chemical Rubber Publishing Company, Cleveland, OH. (1983).

Welcher, F.J., Hahn, R.B., Semimicro Qualitative Analysis, D. Van Nostrand Co., Inc., Princeton, NJ, p. 458. (1955).

Wicks, C.E., et al., Thermodynamic Properties of 65 Elements - Their Oxides, Halides Carbides and Nitrides, PB 196654, Bureau of Mines, Washington, DC. (1963).

Windholz, M., Budavari, S., Stroumtsos, L.Y., Fertig, M.N. (ed.), The Merck Index, Ninth Edition, Merck & Co. Inc., Rahway, NJ. (1976).

Windholz, M., Budavari, S., Blumetti, R.F., Otterbein, E.S. (ed.), The Merck Index, 10th Edition, Merck & Co. Inc., Rahway, NJ. (1983).

Zitko, V., Aiken, D.E., Tibbo, S.W., et al., "Toxicity of Yellow Phosphorus to Herring (*Clupea Harengus*), Atlantic Salmon (*Salmo Salar*), Lobster (*Homarus Americanus*) and Beach Flea (*Gammarus Oceanicus*)", Journal of Fisheries Research Board of Canada, Vol. 27, pp. 21-29. (1970).

EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight